I42

REGISTERED No. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XVIII] *SECTION A* [No. 1

JULY, 1943

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, BANGALORE.

STUDIES IN BLUE PERCHROMIC ACID

Part I—Kinetics of the Decomposition of the Blue Perchromic Acid in Various Organic Media

By Satya Prakash, D.Sc., F.A.Sc.,
and
Ram Chandra Rai, M.Sc.
(*University of Allahabad*)

Received April 30, 1943

Barreswil[1] observed in 1847, that a deep blue solution is produced when a concentrated solution of chromic acid is mixed with hydrogen peroxide. If ether be shaken up with the blue solution, the aqueous layer is decolourised, and the ethereal layer retains the blue product. It was further observed by Grosvenor[2] that the blue compound is also soluble in ethyl acetate, amyl chloride, and various amyl esters. It is insoluble in carbon disulphide, benzene, toluene, carbon disulphide and various oils. The ethereal solution gives dirty violet precipitates with various alkaloids and amines, and when the precipitates are dried and treated with acids and ether, the blue solution is again obtained. Berthelot,[3] moreover, showed that with strong acids and a solution of dichromate, hydrogen peroxide gives the blue colour of the hypothetical blue perchromic acid. With the weaker acids, the colour is violet and not blue. The blue perchromic acid as extracted with ether or ethyl acetate is stable only for a few hours ; it decomposes with the evolution of oxygen. Various attempts have been made by Barreswil, Aschoff,[4] Brodie,[5] Martinon,[6] Berthelot, Riesenfeld,[7] Spitalsky[8] and others to elucidate the nature of this blue perchromic acid. In spite of the extensive work of Riesenfeld and Spitalsky, on the catalytic decomposition, not much work has been done on the kinetics of the decomposition of the blue perchromic acid itself. In the present series of papers, we propose to undertake the study of this blue perchromic acid from various standpoints with an idea to work out the conditions under which the acid is produced, its stability and decompositions, and also the various organic reactions in which the acid may be used.

Preparation of the Blue Acid

In all the experiments recorded in this paper, the blue perchromic acid was prepared from potassium dichromate (5% solution), dilute sulphuric

acid (2 N) and hydrogen peroxide (1·8 N). These solutions, as well as ether, were cooled in ice. 80 c.c. of the dichromate solution were taken in Jena conical flasks, also cooled to the ice temperature, and to this solution were added 20 c.c. of the dilute sulphuric acid. 40 to 50 c.c. of the hydrogen peroxide solution were added to the mixture, and immediately, the reaction mixture was shaken with about 120 c.c. of the ice-cooled ether. The ethereal layer which extracted out the blue perchromic acid was separated out from the aqueous layer by separating funnel. The proper separation was very necessary in the study of the reactions and therefore, all care was taken to ensure it.

The concentration of the blue acid thus extracted depended on the mode of preparation and the quantity of hydrogen peroxide used. The concentrations of the acid were determined in terms of the iodine liberated from potassium iodide in presence of dilute sulphuric acid, the iodine being titrated with hypo (N/20). A known volume of the blue acid was also evaporated to dryness over water-bath, and the residue left was weighed. The residue was further ignited in the platinum crucible and also weighed.

For each set of experiments, the same blue perchromic acid was used for proper comparison. This is necessary, because each preparation of the blue perchromic acid gives the acid of different strengths and characteristics.

The decomposition of the blue acid follows the monomolecular formula, and therefore the velocity constants were determined by the use of the equation :

$$K = \frac{1}{t} \log \frac{a}{a-x} = \frac{2 \cdot 303}{t} \log_{10} \frac{a}{a-x},$$

where a is the initial concentration, and $a - x$ the concentration at the time t.

Influence of Temperature on Decomposition

The 10 c.c. of the blue perchromic acid, prepared by the method given, left a residue of 0·0294 g. when evaporated over water-bath. This residue when ignited in the platinum crucible weighed 0·0198 g. of Cr_2O_3.

Different portions of the same acid were allowed to stand in Jena conical flasks in thermostats maintained at 10°, 20° and 30° ± 0·2. 2 c.c. of the blue acid were pipetted out from time to time, and immediately transferred to potassium iodide solution acidified with dilute sulphuric acid. The iodine liberated was titrated with hypo (N/20).

TABLE I

At 10°			At 20°			At 30°		
Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303
0	4·2		19	4·1		0	4·15	
		0·000443			0·00148			0·00293
60	3·95		39	3·7		15	3·75	
		0·000659			0·00235			0·00560
120	3·5		79	3·1		30	2·8	
		0·000693			0·00210			0·00734
180	3·15		109	2·65		45	2·15	
		0·000670			0·00225			0·00736
240	2·9		139	2·2		60	1·5	
		0·000776			0·00225			0·00718
300	2·45		169	1·85		75	1·2	
		0·000807			0·00234			0·00737
360	2·15		199	1·6		90	0·9	
		0·000847			0·00222			0·00791
420	1·85		229	1·3		105	0·6	
		0·000960			0·00237			
480	1·45		259	1·05				
		0·00100			0·00251			
540	1·2		289	0·85				
		0·00100						
600	1·0							
Average K/2·303 Induction period		0·000923 300 mins.			0·00229 70 mins.			0·00743 40 mins.

The decomposition of blue perchromic acid is very slow at 0° C. ; it takes more than 20 hours to undergo decomposition. At lower temperatures there is a pronounced induction period, and therefore, the monomolecular values of K show also a slight continuous increase with time. At temperatures above 30°, the decomposition is very rapid. The values of log K plotted against inverse temperatures $\left(\frac{1}{T}\right)$ give a straight line, showing that Arrhenius equation is applicable to the decomposition of the blue perchromic acid.

From the results recorded above, it is also seen that there is a marked induction period at low temperatures within which the values of K show a continuous increase.

Decomposition of the Blue Acid in Presence of Benzene

It is known that the blue perchromic acid is not extracted out by benzene, but benzene being miscible with ether, it was found interesting to study the decomposition of the acid in ethereal solution in presence of

benzene. The blue acid was prepared by mixing 80 c.c. of 5% potassium dichromate, 20 c.c. of 2 N sulphuric acid, 50 c.c. of 1·8 N hydrogen peroxide and 120 c.c. of ether. From the ethereal extract of the perchromic acid, the following four combinations were made, keeping the total volume 30 c.c. and maintaining the same concentration of the blue acid. The decompositions of these four combinations at 30° were studied as in the previous experiments.

I—Blue acid 20 c.c. + ether 10 c.c.

II—Blue acid 20 c.c. + benzene 2 c.c. + ether 8 c.c.

III—Blue acid 20 c.c. + benzene 6 c.c. + ether 4 c.c.

IV—Blue acid 20 c.c. + benzene 10 c.c.

TABLE II

No benzene			2 c.c. benzene			6 c.c. benzene			10 c.c. benzene		
Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303
0	7·7	·01026	3	7·65	·01060	6	6·95	·01321	9	5·4	·0124
15	5·4	·00912	18	5·3	·00999	21	4·2	·0134	17·5	4·25	·0138
30	4·1	·00976	34	3·75	·01009	36	2·75	·0133	24	3·35	·0141
45	2·8	·00940	48	2·75	·00999	51	1·7	·0161	32	2·5	·0162
60	2·1	·00987	63	1·95	·01004	66	0·75	·0155	54	1·0	·0188
75	1·4	·00985	78	1·4	·01090	81	0·45	·0162	69	0·5	·0177
90	1·1	·00977	93	0·9	·01050	96	0·3		84	0·25	
105	0·75	·00985	108	0·6	·01040						
120	0·5		123	0·4							
Average K/2·303		·00973			·01031		I II	·0133 ·0159		I II	·0134 ·0175

It will be seen from the results recorded in Table II, that the decomposition of the blue acid is faster in presence of benzene than in ether alone. When the concentration of benzene is increased, it appears as if the decomposition is taking place in two stages : the monomolecular constants of the second stage are larger than those of the first stage. It is very likely that benzene reacts chemically with perchromic acid, and this secondary reaction influences the primary decomposition of the blue acid. The study of the

products formed by the reaction of benzene and perchromic acid is reserved for a subsequent paper.

Decomposition of the Blue Acid in Presence of Toluene

The decomposition kinetics of the blue perchromic acid was studied in presence of toluene also in the same way as in the previous case. The blue acid was prepared and extracted with ether, 10 c.c. of the acid on evaporation on water-bath left a residue of 0·0682 g., and this residue on ignition weighed 0·0448 g. of Cr_2O_3. The decomposition of the following combinations was investigated at 30° C.:

I—Blue acid 20 c.c. + ether 10 c.c.

II—Blue acid 20 c.c. + toluene 2 c.c. + ether 8 c.c.

III—Blue acid 20 c.c. + toluene 6 c.c. + ether 4 c.c.

IV—Blue acid 20 c.c. + toluene 10 c.c.

TABLE III

No toluene			2 c.c. toluene			6 c.c. toluene			10 c.c. toluene		
Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303
0	6·05		3	5·25		6	4·6		9	3·15	
		·00899			·0086			·0165			·0254
15	4·35		18	3·9		21	2·6		14	2·35	
		·01040			·0119			·0188			·0224
30	2·95		33	2·3		36	1·25		24	1·45	
		·00974			·0115			·0188			·0260
45	2·2		48	1·6		51	0·65		29	0·95	
		·00962			·0123			·0168			·0252
60	1·6		63	0·9		66	0·45		39	0·55	
		·00961			·0120						·0241
75	1·15		78	0·65					44	0·45	
		·01000			·0113						·0271
90	0·75		93	0·5					54	0·3	
Average K/2·303		·0097			·0118			·0177			·0250

From these results, it will be seen that monomolecular constants are obtained when the decomposition of perchromic acid takes place in the presence of toluene. With the increased concentrations of toluene, we get an increased value of K.

Decomposition of the Blue Acid in Presence of Xylene

The results on the decomposition kinetics of the blue perchromic acid in presence of xylene are given in Table IV. The blue acid was prepared

in the way already described. 10 c.c. of this acid when dried on water-bath left 0·058 g. of residue which on ignition gave 0·0387 g. of Cr_2O_3. The decomposition of the following combinations was studied at 30°.

I—Blue acid 20 c.c. + ether 10 c.c.

II—Blue acid 20 c.c. + xylene 2 c.c. + ether 8 c.c.

III—Blue acid 20 c.c. + xylene 6 c.c. + ether 4 c.c.

IV—Blue acid 20 c.c. + xylene 10 c.c.

TABLE IV

No xylene			2 c.c. xylene			6 c.c. xylene			10 c.c. xylene		
Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303	Time mins.	Hypo c.c.	K/2·303
0	4·9		3	4·4		6	4·2		9	2·9	
		·0077			·0079			·0097			·0281
15	3·75		18	3·35		21	3·0		14	2·1	
		·0077			·00877			·0107			·0308
30	2·85		33	2·4		36	2·0		24	1·0	
		·0087			·00862			·00931			·0308
45	2·15		48	1·8		51	1·6		29	0·7	
		·00906			·00882			·01003			·0286
60	1·4		63	1·3		66	1·05		39	0·4	
		·00931			·00910			·0096			·0281
75	1·1		78	0·9		81	0·8		44	0·3	
		·0087						·00938			
90	0·8					96	0·6				
Average K/2·303		·00892			·00875			·00976			·02928

In the presence of xylene, perchromic acid decomposition rate is increased. With 2 c.c. of xylene, the change observed is not marked, whereas with 10 c.c. of it, the rate of decomposition increases about three times.

It is very significant to see that the decomposition influence is most prominent in the case of xylene and the least in the presence of benzene. Toluene shows an intermediate behaviour as is shown in the following table:

TABLE V

Hydrocarbon	K_1 in absence of hydrocarbon	K_2 with 10 c.c. hydrocarbon	K_2/K_1
Benzene	·02241	·04030	1·79
Toluene	·02235	·05757	2·57
Xylene	·02054	·06747	3·28

We have observed that along with the decomposition of perchromic acid, traces of aldehydes are formed from toluene and xylene, which give indication with Schiff's reagent. We are also studying the decomposition products of the blue acid.

Summary

The decomposition kinetics of the blue perchromic acid was studied under various conditions. The decomposition reaction is monomolecular. The value of K at 10° is 0·002125, at 20° 0·005273 and at 30° 0·01711 to 0·02241. The values differ slightly with different preparations. The values of log K plotted against 1/T give straight line, showing that Arrhenius equation is valid. From the study of kinetics, we find that there is a marked induction period also.

The rate of decomposition of the blue acid is markedly increased in the presence of benzene, toluene and xylene. When these hydrocarbons are present to the extent of 33 per cent. of the ethereal solution, the values of K increase 1·79 times with benzene, 2·57 times with toluene and 3·28 times with xylene, when the temperature maintained is 30°.

REFERENCES

1. Barreswil .. *Ann. Chim. Phys.*, 1848, **20** (3), 364; *Compt. Rend.*, 1848, **16**, 1085.
2. Grosvenor .. *J. Amer. Cem. Soc.*, 1895, **17**, 41.
3. Berthelot .. *Compt. Rend.*, 1889, **108**, 24, 157, 477.
4. Aschoff .. *Chem. News*, 1862, **5**, 129; *J. prakt. Chem.*, 1860, **81** (1), 402.
5. Brodie .. *Proc. Roy. Soc.* 1861, **11**, 443.
6. Martinon .. *Bull. Soc. Chim.*, 1861, **45** (2), 862.
7. Riesenfeld .. *Z. anorg. Chem.*, 1912, **74**, 48 and various papers in *Berichte* (1906–12).
8. Spitalsky .. *Ibid.*, 1907, **53**, 184; **54**, 184; **57**, 72; 1910, **69**, 169.

SPECTRAL AND COLLISION DATA OF CO^+ AND THE DISSOCIATION ENERGY OF CARBON MONOXIDE

By R. K. Asundi

(College of Science, Benares Hindu University)

Received June 9, 1943

That the energy of dissociation of carbon monoxide, D (CO) cannot be much less than 10 e.v., was shown to be deducible from a number of considerations.[1] Recently, Gaydon and Penney have suggested that D (CO) lies between 9·85 and 11·11 e.v.[2] The spectrum of CO^+ corroborating the data on collision processes further offers some interesting evidence bearing on this subject.

The dissociation energy of CO is 2·9 or 0·55 e.v. more than that of CO^+ according as D (CO^+) = D (CO) + I (C) − I (CO) or D (CO^+) = D (CO) + I (O) − I (CO). The three known electronic states of CO^+ namely X $(^2\Sigma^+)$, A $(^2\Pi)$ and B $(^2\Sigma^+)$ give on linear extrapolation of the vibrational levels, energies of dissociation of 9·9, 6·0 and 3·7 e.v., and therefore dissociation limits of 9·9, 7·9 and 9·3 e.v., from the ground level of CO^+ respectively. The vibrational levels of these states are directly known upto energy values of 25,963 cm.$^{-1}$ or 3·22 e.v., 20,169 cm.$^{-1}$ or 2·5 e.v., and 14,543 cm.$^{-1}$ or 1·8 e.v., respectively.[3] Thus the extrapolation of B state is of the same order of accuracy as that of the ground state of CO. The extrapolation of A is less accurate and that of X looks comparatively long. To avoid further complications in the correlation of dissociation products the latter is generally considerably discounted.

Biskamp has observed perturbations in $v = 7$ level of B state.[4] From calculations made by us these appear to be vibrational perturbations caused by the vibrational levels of X state. Counting from the ground state of CO^+ the energy of X at $v = 33$ is 55,982 cm.$^{-1}$ or 6·9 e.v., and that of B in the seventh vibrational level is 56,330 cm.$^{-1}$ If this interpretation is correct, we practically know the levels of X upto 6·9 e.v. Its extrapolation is then of at least an equal if not greater order of accuracy than of either A and B states of CO^+ or the ground state of CO.

If to the dissociation limits of X, A and B we add I (CO) = 14·1 e.v., we get 24, 22 and 23·4 e.v., respectively. These values can be correlated

to and should be regarded as being in agreement with those obtained by collision experiments,[5] due regard being given to possible inaccuracies in both methods. Thus we identify the first two with $23{\cdot}3 \pm 0{\cdot}2$ and $20{\cdot}9 \pm 0{\cdot}2$ e.v. which are already attributed to the dissociation processes involving products $C\,(^3P) + O^+\,(^4S)$ and $C^+\,(^2P) + O\,(^3P)$ respectively. The third is identical with $22{\cdot}8 \pm 0{\cdot}2$ e.v., and represents the process in which a further excitation of O from ^3P to ^1D occurs in the second process. This is evident because the minimum spectroscopic value for the dissociation limit of B being already $1{\cdot}8 + 5{\cdot}64 = 7{\cdot}44$ e.v., it is hardly possible to correlate it with that of the A state. It must therefore involve an excited O atom 1·93 e.v., $(^1D - {}^3P)$, above the limit of A. Also the limit of X should be 2·35 e.v., $\{I\,(O) - I\,(C)\}$, above the limit of A. We thus conclude from spectral and collision data taken together that X is derived from $C\,(^3P) + O^+\,(^4S)$, A from $C^+\,(^2P) + O\,(^3P)$ and B from $C^+\,(^2P) + O\,(^1D)$.

Such a possibility has been already indicated on other grounds.[6] Atom or ion collision experiments are also interesting for this conclusion. The process $CO^+ \rightarrow C^+ + O$ is found to be particularly intense while $CO^+ \rightarrow C + O^+$ is weak and not certain.[7] This is probably due to the circumstance that in such type of collisions, processes involving comparatively large changes in internuclear distances are likely to be more favoured. This distance r_e for $X\,(^1\Sigma)$ of CO is 1·13 A., while r_e values for X, A* and B states of CO^+ are 1·114, 1·195—1·209 and 1·168 A., respectively. Thus in these experiments it is $A\,(^2\Pi)$ which is directly reached by collision.

All these considerations show that only the extrapolation of state A is not very reliable. A glance at the values for this state deduced by various authors (namely 13·30 Herzberg,[8] 14·07 Weizel, Jevons and Sponer: Reports) confirms this suspicion. We, therefore, believe that the dissociation limits for X, A and B states deducible from spectroscopic data are 9·9, 7·5 and 9·4 e.v., respectively. These yield for D (CO) the values 10·45 e.v., from X state and 10·4 e.v., from A state, values which are remarkably close. From collision data on similar interpretation, we obtain 9·2, 6·8 and 8·7 e.v., respectively yielding for D (CO) 9·75 e.v., from X and 9·7 e.v., from A. The mean of these four values is 10·1 e.v.

Anand has recently reported two Rydberg series in emission in the extreme short-wave spectrum of CO and deduces 14·5 e.v., as their common limit.[9] If the interpretation is correct, the limit can only refer to the

* The values for the doublet state A quoted in the literature are evidently calculated on the wrong basis of regarding the (3, 0) comet-tail band as the (0, 0) band. The values quoted here are accordingly corrected.

X state of CO^+, in which case the D (CO) spectroscopic value will have to be increased by 0·4 e.v.

REFERENCES

1. Asundi and Samuel, *Proc. Ind. Acad. Sci.*, 1936, **3**, 526.
2. Gaydon and Penney, *Nature*, 1942, **150**, 406.
3. Data from Sponer, except the excitation potential for A ($^2\Pi$) which is from Asundi, *Curr. Sci.*, 1940, **9**, 503.
4. Biskamp, *Zeit. f. Phys.*, 1933, **86**, 33.
5. Hagstrum and Tate, *P. R.*, 1941, **59**, 354.
6. Asundi and Samuel, *Proc. Ind. Acad. Sci.*, 1937, **5**, 235.
7. Friedlander and others, *Zeit. f. Phys.*, 1932, **76**, 62.
8. Herzberg, *ibid.*, 1929, **52**, 815.
9. Anand, *Sc. and Cult.*, 1942, **8**, 278.

SOME INTEGRALS INVOLVING HUMBERT FUNCTION

By B. R. Pasricha*

(Isabella Thoburn College, Lucknow)

Received September 26, 1942

(Communicated by Prof. B. S. Madhava Rao, D.Sc., F.A.Sc.)

1. Humbert† introduced in the year 1930 the function $J_{m,n}(x)$ defined by

$$J_{m,n}(x) = \frac{x^{m+n}}{3^{m+n}\,\Gamma(m+1)\,\Gamma(n+1)}\,{}_0F_2\left(m+1,\, n+1;\, -\frac{x^3}{27}\right). \quad (1)$$

He has given‡ the following form for the operational image of this function

$$\frac{1}{p^{m-\frac{1}{2}n}}\,J_n\left(-2\sqrt{\frac{1}{p}}\right) \subset x^{\frac{2m-n}{3}}\,J_{m,n}(3\sqrt[3]{x}). \quad (2)$$

The object of this paper is to investigate, by the method of operational calculus, some integrals involving the product of two Humbert functions.‖

2. Putting $z = \left(-2\sqrt{\frac{1}{p}}\right)$ in the known result¶

$$\left(\frac{1}{2}z\right)^{k-m-n} J_m(az)\,J_n(bz) = \frac{a^m b^n}{\Gamma(m+1)\,\Gamma(n+1)} \sum_{r=0}^{\infty} \frac{\Gamma(k+2r)\,\Gamma(k+r)}{r!}\,J_{k+2r}(z)$$
$$\times F_4(-r,\, k+r;\, m+1,\, n+1;\, a^2,\, b^2)$$

where F_4 denotes the Appell's function defined by

$$F_4(\alpha, \beta;\, \gamma, \gamma';\, x, y) = \sum_{m=0}^{\infty} \frac{(\alpha, m)\,(\beta, m)}{(\gamma, m)\,(1, m)}\,F(\alpha+m, \beta+m;\, \gamma';\, y)\,x^m \quad (3)$$

---

* I am deeply indebted to Dr. R. S. Varma for suggesting this problem to me and for his guidance in the preparation of this paper.

† P. Humbert, "Les fontions de Bessel du triosieme ordre," *Atti Pont Acad. della Scienza*, (Sess III del 16 Febbraio, 1930), **Anno 83**, 128-46.

‡ P. Humbert, "Nouvelles remarques sur les fontions de Bessel du triosieme ordre," *ibid.*, (Sess IV del 18 Marxo, 1934), **Anno 87**, 323-31.

§ I have followed Dr. McLachlan in using the symbol $\subset$ for the operational image of a function.

‖ The name Humbert Functions as already adopted by Dr. R. S. Varma instead of Bessel Functions of the 3rd order has been preferred as the latter name is associated with functions of a different type.

¶ W. N. Bailey, *Quar. Journ. of Math.* (Oxford Series), 1935, **6**, 235.

and then multiplying either side by $\frac{a^{2l-m}\, b^{2l'-n}}{p^{1+l+l'-\frac{1}{2}k}}$, we have

$$\frac{1}{p}\cdot\frac{1}{\left(\frac{p}{a^2}\right)^{l-\frac{1}{2}m}} J_m\left(-2\sqrt{\frac{a^2}{p}}\right)\frac{1}{\left(\frac{p}{b^2}\right)^{l'-\frac{1}{2}n}} J_n\left(-2\sqrt{\frac{b^2}{p}}\right)$$

$$= \frac{(-)^{m+n-k}\, a^{2l}\, b^{2l'}}{\Gamma(m+1)\,\Gamma(n+1)} \sum_{r=0}^{\infty} \frac{\Gamma(k+2r)\,\Gamma(k+r)}{r!} \times \frac{1}{(p)^{\frac{2(1+l+l'+r)-(k+2r)}{2}}} J_{k+2r}\left(-2\sqrt{\frac{1}{p}}\right) \times F_4(-r, k+r;\ m+1, n+1;\ a^2, b^2). \qquad (4)$$

Now we know* that if $\phi(p) \subset f(x)$

then $\phi(p/s) \subset f(sx)$ $\quad s = \text{const.} > 0.$

Applying this to (2) we have

$$\frac{1}{\left(\frac{p}{a^2}\right)^{l-\frac{1}{2}m}} J_m\left(-2\sqrt{\frac{a^2}{p}}\right) \subset (a^2x)^{\frac{2l-m}{3}} J_{l,m}(3\sqrt[3]{a^2x})$$

and

$$\frac{1}{\left(\frac{p}{b^2}\right)^{l'-\frac{1}{2}n}} J_n\left(-2\sqrt{\frac{b^2}{p}}\right) \subset (b^2x)^{\frac{2l'-n}{3}} J_{l',n}(3\sqrt[3]{b^2(x)})$$

These together with the product theorem,* *viz.*,

if $\phi_1(p) \subset f_1(x)$ and $\phi_2(p) \subset f_2(x)$

then $\frac{1}{p}\phi_1(p)\,\phi_2(p) \subset \int_0^x f_1(t)\, f_2(x-t)\, dt$

give us the original of L.H.S. of (4) to be

$$\int_0^x (a^2t)^{\frac{2l-m}{3}} [b^2(x-t)]^{\frac{2l'-n}{3}} J_{l,m}(3\sqrt[3]{a^2t})\, J_{l',n}[3\sqrt[3]{b^2(x-t)}]\, dt.$$

The original of R.H.S. of (4), obtained by term by term interpretation with the help of (2), is

$$\frac{(-)^{m+n-k}\, a^{2l}\, b^{2l'}\, x^{\frac{2(1+l+l')-k}{3}}}{\Gamma(m+1)\,\Gamma(n+1)} \sum_{r=0}^{\infty} \frac{\Gamma(k+2r)\,\Gamma(k+r)}{r!} J_{1+l+l'+r,\ k+2r}(3\sqrt[3]{x}) \times F_4(-r, k+r;\ m+1, n+1;\ a^2, b^2)$$

* Carson, *Electric Circuit Theory and Operational Calculus* (McGraw Hill, New York, 1936).

Hence Lerch's theorem gives that

$$\int_0^x (a^2t)^{\frac{2l-m}{3}} [b^2(x-t)]^{\frac{2l-n}{3}} J_{l,m}(3\sqrt[3]{a^2t})\, J_{l',n}[3\sqrt[3]{b^2(x-t)}]\, dt$$

$$= \frac{(-)^{m+n-k} a^{2l} b^{2l'} x^{\frac{2(1+l+l')-k}{3}}}{\Gamma(m+1)\,\Gamma(n+1)} \sum_{r=0}^{\infty} \frac{\Gamma(k+2r)\,\Gamma(k+r)}{r!} J_{1+l+l'+r,\,k+2r}(3\sqrt[3]{x})$$

$$\times F_4(-r, k+r;\ m+1, n+1;\ a^2, b^2). \qquad (5)$$

3. It is easy to see that the known relation*

$$(A)\quad \left(\frac{1}{2}bz\right)^{m-n} J_n(bz) = b^m \sum_{r=0}^{\infty} \frac{\Gamma(m+r)}{r!\,\Gamma(n+r)} F(m+r, -r; n+1; k^2) \times (n+2r)\, J_{m+2r}(z)$$

by the above method gives the result†

$$J_{l,n}(3\sqrt[3]{b^2x}) = (-)^{n-m} b^{\frac{2}{3}(l+n)} x^{\frac{1}{3}(n-m)} \sum_{r=0}^{\infty} \frac{\Gamma(m+r)}{r!\,\Gamma(n+1)} (n+2r)\, J_{l+r,\,m+2r}(3\sqrt[3]{x}) \times F(m+r, -r; n+1; k^2) \qquad (6)$$

and that the known relation‡

$$(B)\quad \left(\frac{1}{2}z\right)^{k-m-n} J_m(az)\, J_n(bz) = \frac{a^m b^n\, \Gamma(k+1)}{\Gamma(m+1)\,\Gamma(n+1)} \sum_{r=0}^{\infty} \frac{(\frac{1}{2}z)^r}{r!} J_{k+r}(z) \times F_4(-r, k+1;\ m+1, n+1;\ a^2, b^2)$$

gives the result

$$\int_0^x (a^2t)^{\frac{2l-m}{3}} J_{l,m}(3\sqrt[3]{a^2t})\, [b^2(x-t)]^{\frac{2l'-n}{3}} J_{l',n}[3\sqrt[3]{b^2(x-t)}]\, dt$$

$$= \frac{(-)^{m+n-K}\,\Gamma(k+1)\, a^{2l} b^{2l'} x^{\frac{2(l+l+l')-K}{3}}}{\Gamma(m+1)\,\Gamma(n+1)} \sum_{r=0}^{\infty} \frac{(-)^r x^{r/3}}{r!} J_{1+l+l'+r,\,k+r}(3\sqrt[3]{x})$$

$$\times F_4(-r, k+1;\ m+1, n+1;\ a^2, b^2). \qquad (7)$$

4. As another illustration of the above method we, by putting $z = \left(-2\sqrt{\frac{1}{p}}\right)$ in

---

* Watson, *Bessel Functions* (Camb. Univ. Press, 1922), p. 140.

† This result has been included here because it gives the expansion of a Humbert function in an infinite series involving Humbert functions.

‡ Bailey, *loc. cit.*

$$J_m(z)\,J_n(z) = \frac{1}{\Gamma(m+1)\,\Gamma(n+1)}\left(\frac{z}{2}\right)^{m+n} {}_2F_3\left(\begin{matrix}\frac{1+m+n}{2}, & \frac{2+m+n}{2}\\ 1+m, 1+n, 1+m+n;\end{matrix} -z^2\right),^*$$

get that

$$\frac{1}{p}\cdot\frac{1}{p^{\frac{2a-m}{2}}}J_m\left(-2\sqrt{\frac{1}{p}}\right)\cdot\frac{1}{p^{\frac{2a'-n}{2}}}J_n\left(-2\sqrt{\frac{1}{p}}\right)$$

$$= \frac{(-)^{m+n}}{\Gamma(m+1)\,\Gamma(n+1)\,p^{1+a+a'}}\,{}_2F_3\left(\begin{matrix}\frac{1+m+n}{2}, & \frac{2+m+n}{2};\\ 1+m, 1+n, 1+m+n;\end{matrix} -\frac{4}{p}\right) \quad (8)$$

The original of L.H.S. of this is evidently

$$\int_0^x t^{\frac{2a-m}{3}}(x-t)^{\frac{2a'-n}{3}} J_{a,m}(3\sqrt[3]{t})\,J_{a',n}(3\sqrt[3]{x-t})\,dt.$$

R.H.S. of (8)

$$= \frac{(-)^{m+n}}{\Gamma(m+1)\,\Gamma(n+1)}\sum_{r=0}^{\infty}\frac{\left(\frac{1+m+n}{2}, r\right)\left(\frac{2+m+n}{2}, r\right)}{r!\,(1+m, r)\,(1+n, r)\,(1+m+n, r)}\times\frac{(-4)^r}{p^{1+a+a'+r}}$$

$$\subset \frac{(-)^{m+n}}{\Gamma(m+1)\;\Gamma(n+1)}\sum_{r=0}^{\infty}\frac{\left(\frac{1+m+n}{2}, r\right)\left(\frac{2+m+n}{2}, r\right)}{r!\,(1+m, r)\,(1+n, r)\,(1+m+n, r)}\times\frac{(-4)^r\,x^{1+a+a'+r}}{\Gamma(2+a+a'+r)}$$

$$= \frac{(-)^{m+n}\,x^{1+a+a'}}{\Gamma(m+1)\;\Gamma(n+1)\;\Gamma(2+a+a')}\,{}_2F_4\left(\begin{matrix}\frac{1+m+n}{2}, & \frac{2+m+n}{2};\\ 1+m, 1+n, 1+m+n, 2+a+a';\end{matrix} -4x\right).$$

Hence

$$\int_0^x t^{\frac{2a-m}{3}}(x-t)^{\frac{2a'-n}{3}} J_{a,m}(3\sqrt[3]{t})\,J_{a',n}(3\sqrt[3]{x-t})\,dt$$

$$= \frac{(-)^{m+n}\,x^{1+a+a'}}{\Gamma(m+1)\,\Gamma(n+1)\,\Gamma(2+a+a')}\,{}_2F_4\left(\begin{matrix}\frac{1+m+n}{2}, & \frac{2+m+n}{2};\\ 1+m, 1+n, 1+m+n, 2+a+a';\end{matrix} -4x\right) \quad (9)$$

The following cases in which the function on the R.H.S. of the general result (9) reduces to Humbert function deserve special mention:

---

* Whittaker and Watson, *Modern Analysis* (4th Ed.), p. 380.

I. Taking $(1+m+n)/2 = 1+m$ and $(2+m+n)/2 = 1+m+n$, we have

$$\int_0^x t^{\frac{4a+1}{6}} (x-t)^{\frac{4a'-1}{6}} J_{a,-\frac{1}{2}}(3\sqrt[3]{t})\, J_{a',\frac{1}{2}}(3\sqrt[3]{x-t})\, dt$$

$$= \frac{x^{\frac{1}{3}(a+a')+\frac{1}{2}}}{\sqrt{\pi}\, 2^{\frac{1}{3}(a+a')+1}} J_{\frac{1}{2},\, 1+a+a'}(3\sqrt[3]{4x}) \qquad (10)$$

II. Taking $(1+m+n)/2 = 1+m$ and $(2+m+n)/2 = 2+a+a'$, we get that

$$\int_0^x t^{\frac{2a-2a'-1}{6}} J_{a,\, a+a'+\frac{1}{2}}(3\sqrt[3]{t})\, (x-t)^{\frac{2a'-2a-3}{6}} J_{a',\, a+a'+\frac{3}{2}}(3\sqrt[3]{x-t})\, dt$$

$$= \frac{(-)^{2(a+a')}}{\sqrt{\pi}\, 2^{1/3}\, x^{1/6}} J_{a+a'+\frac{3}{2},\, 2(1+a+a')}(3\sqrt[3]{4x}) \qquad (11)$$

III. If $(1+m+n)/2 = 1+m+n$ and $(2+m+n)/2 = 1+n$, then

$$\int_0^x t^{\frac{4a+1}{6}} (x-t)^{\frac{4a'+1}{6}} J_{a,-\frac{1}{2}}(3\sqrt[3]{t})\, J_{a',-\frac{1}{2}}(3\sqrt[3]{x-t})\, dt.$$

$$= -\frac{x^{\frac{1}{3}(a+a')+\frac{5}{6}}}{\sqrt{\pi}\, 2^{\frac{1}{3}(a+a')+\frac{1}{3}}} J_{-\frac{1}{2},\, 1+a+a'}(3\sqrt[3]{4x}) \qquad (12)$$

IV. Taking $(1+m+n)/2 = 2+a+a'$ and $(2+m+n)/2 = 1+n$, we have

$$\int_0^x t^{\frac{2a-2a'-3}{6}} J_{a,\, a+a'+3/2}(3\sqrt[3]{t})\, (x-t)^{\frac{2a'-2a-3}{6}} J_{a',\, a+a'+3/2}(3\sqrt[3]{x-t})\, dt$$

$$= \frac{(-)^{2a+2a'+1}}{\sqrt{\pi x}} J_{a+a'+\frac{3}{2},\, 2a+2a'+3}(3\sqrt[3]{4x}) \qquad (13)$$

V. Two more cases are possible when $a+a'+(3/2) = 0$.

(i) If $(1+m+n)/2 = 1+m+n$ and $(2+m+n)/2 = 2+a+a'$, we have

$$\int_0^x t^{\frac{2a-m}{3}} J_{a,m}(3\sqrt[3]{t})\, (x-t)^{\frac{m-2a-2}{3}} J_{-a-3/2,\,-(1+m)}(3\sqrt[3]{x-t})\, dt$$

$$= -\frac{2^{2/3}}{\sqrt{\pi}\, x^{1/6}} J_{m,\,-(1+m)}(3\sqrt[3]{4x}) \qquad (14)$$

(ii) Taking $(1+m+n)/2 = 2+a+a'$ and $(2+m+n)/2 = 1+m+n$,

we get

$$\int_0^x t^{\frac{2a-m}{3}} J_{a,m}(3\sqrt[3]{t})\,(x-t)^{\frac{m-2a-3}{3}} J_{-a-3/2,-m}(3\sqrt[3]{x-t})\,dt$$

$$= \frac{1}{\sqrt{\pi x}} J_{m,-m}(3\sqrt[3]{4x}), \tag{15}$$

provided that in these two results m is not an integer.

5. When the above method with the substitution $z = \frac{1}{p^2}$ is applied to

$${}_1F_1(\alpha;\rho;z) \times {}_1F_1(\alpha;\rho;-z) = {}_2F_3(\alpha, \rho-\alpha;\rho, \tfrac{1}{2}\rho, \tfrac{1}{2}\rho+\tfrac{1}{2};\tfrac{1}{4}z^2)^*$$

we get the result

$$\int_0^x {}_1F_3\left(\begin{matrix}\alpha;\\ \rho, \frac{1}{2}, 1;\end{matrix}\frac{t^2}{4}\right) \times {}_1F_3\left(\begin{matrix}\alpha;\\ \rho, \frac{1}{2}, 1;\end{matrix}-\left(\frac{x-t}{2}\right)^2\right) dt$$

$$= x\ {}_2F_7\left(\begin{matrix}\alpha, \rho-\alpha;\\ \rho, \frac{1}{2}\rho, \frac{1}{2}\rho+\frac{1}{2}, \frac{1}{2}, \frac{3}{4}, 1, \frac{5}{4};\end{matrix}\frac{x^4}{1024}\right) \tag{16}$$

We shall here also note three special cases—

(i) If $\alpha = \rho$,

$$\int_0^x [-t^2(x-t)^2]^{1/6} J_{-\frac{1}{2},0}\left(3\sqrt[3]{-\frac{t^2}{4}}\right) \times J_{-\frac{1}{2},0}\left[3\left(\frac{x-t}{2}\right)^{2/3}\right] dt = \frac{x\,2^{2/3}}{\pi} \tag{17}$$

(ii) when $\alpha = 1/2$,

$$\int_0^x [-t^2(x-t)^2]^{\frac{1-\rho}{3}} J_{-1+\rho,0}\left[3\sqrt[3]{\frac{-t^2}{4}}\right] \times J_{-1+\rho,0}\left[3\left(\frac{x-t}{2}\right)^{2/3}\right] dt$$

$$= \frac{x}{(\Gamma\rho)^2\, 2^{\frac{4}{3}(\rho-1)}}\ {}_1F_6\left(\begin{matrix}\rho-\frac{1}{2};\\ \rho, \frac{1}{2}\rho, \frac{1}{2}\rho+\frac{1}{2}, \frac{3}{4}, 1, \frac{5}{4};\end{matrix}\frac{x^4}{1024}\right) \tag{18}$$

(iii) taking $\alpha = 1$ we have

$$\int_0^x [-t^2(x-t)^2]^{\frac{1}{2}-\rho/3} J_{\rho-1,-\frac{1}{2}}\left(3\sqrt[3]{\frac{-t^2}{4}}\right) J_{\rho-1,-\frac{1}{2}}\left[3\left(\frac{x-t}{2}\right)^{2/3}\right] dt$$

$$= \frac{4x}{\{\Gamma(\rho)\}^2\, \pi\, 2^{\frac{4}{3}\rho}}\ {}_1F_6\left(\begin{matrix}\rho-1;\\ \rho, \frac{1}{2}\rho, \frac{1}{2}\rho+\frac{1}{2}, \frac{1}{2}, \frac{3}{4}, \frac{5}{4};\end{matrix}\frac{x^4}{1024}\right) \tag{19}$$

---

* Bailey, "Products of generalised hypergeometric series," *Proc. Lond. Math. Soc.*, 1928, (2), **28**, 242–54.

6. The same operator $z=\frac{1}{p^2}$ when applied to the known result*

$$
\begin{aligned}
&{}_1F_1(a;\rho;x)\times{}_1F_1(a-\rho+1;2-\rho;-x)\\
&\quad={}_2F_3\left(\begin{matrix}a-\frac{1}{2}\rho+\frac{1}{2},\ \frac{1}{2}\rho-a+\frac{1}{2};\\ \frac{1}{2}\rho+\frac{1}{2},\ \frac{1}{2},\ \frac{3}{2}-\frac{1}{2}\rho;\end{matrix}\ \tfrac{1}{4}x^2\right)+\frac{(2a-\rho)(1-\rho)\,x}{\rho(2-\rho)}\\
&\quad\times{}_2F_3\left(\begin{matrix}a-\frac{1}{2}\rho+1,\ \frac{1}{2}\rho-a+1;\\ \frac{1}{2}\rho+1,\ \frac{3}{2},\ 2-\frac{1}{2}\rho;\end{matrix}\ \tfrac{1}{4}x^2\right)
\end{aligned}
$$

gives the result

$$
\begin{aligned}
&\int_0^x {}_1F_3\left(\begin{matrix}a;\\ \rho,\ \frac{1}{2},\ 1;\end{matrix}\ \frac{t^2}{4}\right)\times{}_1F_3\left[\begin{matrix}a-\rho+1;\\ 2-\rho,\ \frac{1}{2},\ 1;\end{matrix}\ -\left(\frac{x-t}{2}\right)^2\right]dt\\
&\quad=x\ {}_2F_7\left(\begin{matrix}a-\frac{1}{2}\rho+\frac{1}{2},\ \frac{1}{2}\rho-a+\frac{1}{2};\\ \frac{1}{2}\rho+\frac{1}{2},\ \frac{1}{2},\ \frac{3}{2}-\frac{1}{2}\rho,\ \frac{1}{2},\ \frac{3}{4},\ 1,\ \frac{5}{4};\end{matrix}\ \frac{x^4}{1024}\right)+\frac{(2a-\rho)(1-\rho)x^3}{6\rho(2-\rho)}\\
&\qquad\times{}_2F_7\left(\begin{matrix}a-\frac{1}{2}\rho+1,\ \frac{1}{2}\rho-a+1;\\ \frac{1}{2}\rho+1,\ \frac{3}{2},\ 2-\frac{1}{2}\rho,\ 1,\ \frac{5}{4},\ \frac{3}{2},\ \frac{7}{4};\end{matrix}\ \frac{x^4}{1024}\right)
\end{aligned}
\tag{20}
$$

As in § 5 four particular cases deserve attention:

I. (i) $a=\rho$,

$$
\begin{aligned}
&\int_0^x (-t^2)^{\frac{1}{6}}(x-t)^{\frac{2\rho-1}{3}}J_{-\frac{1}{2},0}\left(3\sqrt[3]{\frac{-t^2}{4}}\right)J_{1-\rho,-\frac{1}{2}}\left[3\left(\frac{x-t}{2}\right)^{2/3}\right]dt.\\
&\quad=\frac{2^{\frac{2\rho}{3}}\,x}{\Gamma(2-\rho)\,\pi}\,{}_1F_6\left(\begin{matrix}-\frac{1}{2}\rho+\frac{1}{2};\\ \frac{1}{2},\ \frac{3}{2}-\frac{1}{2}\rho,\ \frac{1}{2},\ \frac{3}{4},\ 1,\ \frac{5}{4};\end{matrix}\ \frac{x^4}{1024}\right)+\frac{2^{\frac{2\rho-3}{3}}\,x^3(1-\rho)}{3\pi\ \Gamma(3-\rho)}\\
&\qquad\times{}_1F_6\left(\begin{matrix}-\frac{1}{2}\rho+1;\\ \frac{3}{2},\ 2-\frac{1}{2}\rho,\ 1,\ \frac{5}{4},\ \frac{3}{2},\ \frac{7}{4};\end{matrix}\ \frac{x^4}{1024}\right)
\end{aligned}
\tag{21}
$$

(ii) If $a=1$,

$$
\begin{aligned}
&\int_0^x (-t^2)^{\frac{1}{2}-\frac{1}{3}\rho}(x-t)^{\frac{1}{3}}\,J_{\rho-1,\,-\frac{1}{2}}\left(3\sqrt[3]{\frac{-t^2}{4}}\right)J_{-\frac{1}{2},0}\left[3\left(\frac{x-t}{2}\right)^{2/3}\right]dt\\
&\quad=\frac{x}{\pi\ \Gamma(\rho)\ 2^{\frac{2}{3}\rho-\frac{4}{3}}}\,{}_1F_6\left(\begin{matrix}-\frac{1}{2}+\frac{1}{2}\rho;\\ \frac{1}{2}\rho+\frac{1}{2},\ \frac{1}{2},\ \frac{1}{2},\ \frac{3}{4},\ 1,\ \frac{5}{4};\end{matrix}\ \frac{x^4}{1024}\right)\\
&\quad+\frac{x^3(1-\rho)}{3\pi\ \Gamma(1+\rho)\ 2^{\frac{2}{3}\rho-\frac{1}{3}}}\,{}_1F_6\left(\begin{matrix}\frac{1}{2}\rho;\\ \frac{1}{2}\rho+1,\ \frac{3}{2},\ 1,\ \frac{5}{4},\ \frac{3}{2},\ \frac{7}{4};\end{matrix}\ \frac{x^4}{1024}\right)
\end{aligned}
\tag{22}
$$

* Bailey, *ibid.*

II. (i) If $\alpha = 1/2$,

$$\int_0^x (-t^2)^{\frac{1}{3}(1-\rho)} J_{\rho-1,0}\left(3\sqrt[3]{\frac{-t^2}{4}}\right) \times {}_1F_3\left[\begin{matrix}\frac{3}{8}-\rho \\ 2-\rho,\ \frac{1}{2},\ 1;\end{matrix} -\left(\frac{x-t}{2}\right)^2\right] dt$$

$$= \frac{x}{\Gamma(\rho)\, 2^{\frac{1}{3}(\rho-1)}}\, {}_2F_7\left(\begin{matrix}1-\frac{1}{2}\rho,\ \frac{1}{2}\rho; \\ \frac{1}{2}\rho+\frac{1}{2},\ \frac{1}{2},\ \frac{3}{8}-\frac{1}{2}\rho,\ \frac{1}{2},\ \frac{3}{4},\ 1,\ \frac{5}{4};\end{matrix} \frac{x^4}{1024}\right)$$

$$+ \frac{x^3(1-\rho)^2}{3\Gamma(1+p)(2-\rho)\, 2^{\frac{1}{3}\rho+\frac{1}{3}}}\, {}_2F_7\left(\begin{matrix}\frac{3}{8}-\frac{\rho}{3},\ \frac{1}{2}\rho+\frac{1}{2}; \\ \frac{1}{2}\rho+1,\ \frac{3}{8},\ 2-\frac{1}{2}\rho,\ 1,\ \frac{5}{4},\ \frac{3}{8},\ \frac{7}{4};\end{matrix} \frac{x^4}{1024}\right) \qquad (23)$$

(ii) If $\alpha = \rho - \frac{1}{2}$,

$$\int_0^x {}_1F_3\left(\begin{matrix}\rho-\frac{1}{2}; \\ \rho,\ \frac{1}{2},\ 1;\end{matrix} \frac{t^4}{4}\right)(x-t)^{\frac{1}{3}\rho-\frac{1}{3}}\, J_{1-\rho,0}\left[3\left(\frac{x-t}{2}\right)^{2/3}\right] dt$$

$$= \frac{x\, 2^{\frac{1}{3}\rho-\frac{2}{3}}}{\Gamma(2-\rho)} \cdot {}_2F_7\left(\begin{matrix}\frac{1}{2}\rho;\ 1-\frac{1}{2}\rho \\ \frac{1}{2}\rho+\frac{1}{2},\ \frac{1}{2},\ \frac{3}{8}-\frac{1}{2}\rho,\ \frac{1}{2},\ \frac{3}{4},\ 1,\ \frac{5}{4};\end{matrix} \frac{x^4}{1024}\right) - \frac{x^3(1-\rho)^2}{3\rho\ \Gamma(3-\rho)}$$

$$\times \frac{1}{2^{\frac{5}{3}-\frac{1}{3}\rho}}\, {}_2F_7\left(\begin{matrix}\frac{1}{2}\rho+\frac{1}{2},\ \frac{3}{8}-\frac{1}{2}\rho; \\ \frac{1}{2}\rho+1,\ \frac{3}{8},\ 2-\frac{1}{2}\rho,\ 1,\ \frac{5}{4},\ \frac{3}{8},\ \frac{7}{4};\end{matrix} \frac{x^4}{1024}\right). \qquad (24)$$

7. It remains to discuss the convergence of the infinite series occurring in results (5)—(7).

Taking the result (5) we have the general term* of F_4 to be less than

$$\sum_{\mu=0}^{\infty} \mu^{2s+k-2}(a+b)^{2\mu},\ s \text{ is} + \text{ive and} > -m \text{ and} - n.$$

Further

$$J_{1+l+l'+r,\ k+2r}(3\sqrt[3]{x}) = \left[\frac{x^{r+\frac{1}{3}(1+l+l'+k)}}{\Gamma(2+l+l'+r)\ \Gamma(1+k+2r)}\right] \times [1+0(r^{-2})]$$

Using this and the Stirling's formula

$$\Gamma(x) = x^{x-\frac{1}{2}}\, e^{-x}\, (2\pi)^{\frac{1}{2}}\, e^{\theta/(12x)}, \qquad 0 < \theta < 1$$

we† have

$$\frac{\Gamma(k+2r)\ \Gamma(k+r)}{r!}\ x^{\frac{1}{3}(1+l+l')-\frac{1}{3}k}\ J_{1+l+l'+r,\ k+2r}(3\sqrt[3]{x}).$$

$$= O\left[\frac{(xe)^r}{r^{r+l+l'-k+7/2}}\right]$$

---

* W. N. Bailey, "Generalized Hypergeometric Series" (*Cambridge Tracts in Mathematics and Mathematical Physics*, No. 32, 1935), p. 75.

† Dr. R. S. Varma, "On Humbert Functions," *Annals of Math.*, 1941, **42**, 429-36.

These give that the series on the right of (5) is less than

$$(-)^{m+n-K} \frac{a^{2l} b^{2l'} x^{1+l+l'}}{\Gamma(m+1)\ \Gamma(n+1)} \sum_{r=0}^{\infty} \frac{(xe)^r}{r!\,\Gamma(r+l+l'-K+1)} \sum_{\mu=0}^{\infty} \mu^{2s+K-2} (a+b)^{2\mu}$$

which is convergent when $(a+b) < 1$.

Hence the infinite series on the right of (5) is convergent under the condition stated just above.

The series on the right of (7) also converges under the same condition.

Further it is easy to see that the general term of the series on the right of (6)

$$= O\left[\frac{(-x k^2 e^2)^r}{r^{2r+l+m+1}}\right]$$

and accordingly the series is convergent.

DYNAMICS OF THUNDERSTORMS*

By S. L. Malurkar

Received 5, 1943

Thunderstorms are of such frequent occurrence and are of such great importance in meteorology, that every attempt at clarification of the processes involved would have a sufficient justification. It is but natural that the thermodynamic aspect has taken the major portion of the discussions on the subject, as energy in the form of heat plays a large role in the phenomenon. The dynamical aspect of the convective currents is also vital to the production of the thunderstorm and an enquiry into it is called for.

The preliminary background was obtained by an examination of the actual upper air soundings made at Poona. The occasions when successful soundings have been made during thunderstorms at a given place are small and the number of observations during the successive development of a thunderstorm still less. The limitation set by the number of observations at a place on days of thunderstorms can be overcome by assuming that the meteorological conditions existing at stations in the neighbourhood of places recording thunderstorms give a fairly good picture of conditions before the onset of thunderstorms. The analysis yielded the following ideas:—

(*a*) In general, the potential temperature of air increased with height, *i.e.*, the lapse rate was less than dry adiabatic. But on certain days, the rise of potential temperature with height was less marked and in some cases there was no appreciable rise for a thickness of one or two kilometres, *i.e.*, the lapse rate was or very nearly was dry adiabatic. On the days when the lapse rate was nearly dry adiabatic, there was a tendency for thunderstorms to occur in the neighbourhood of Poona.

(*b*) However, when the lapse rate was nearly adiabatic and the humidity of air small the distribution of thunderstorms was poor or absent.

(*c*) The air was not necessarily saturated in the lower layers of the atmosphere on days of thunderstorms.

The development of a thunderstorm which is essentially a convective phenomenon needs *a cause for initial convection and then a possibility of its maintenance once the convection has been started.*

---

* Substance of a colloquium given at the Meteorological Office, Poona, in March 1934.

There has been considerable discussion in meteorological literature regarding the existence of potentially colder air superposed over potentially warmer air. If this superposition existed, it may be argued that the system being unstable, may initiate convection and even possibly maintain it. It is theoretically conceivable to have small isolated masses of air which may be potentially colder than the air below it. But it is not evident, whether it is ever possible to have a potentially colder stratum of air superposed over a potentially warmer one for any considerable area or over a long period. Further if such a superposition has once existed for some time, due to certain boundary conditions, it may not give rise to upward motion by itself. A slight digression on this point may not be out of place.

Rayleigh[1] showed as a result of Bernard's experiments, that in shallow layer of liquid the temperature of the lower surface could be increased above the temperature of the top surface upto a certain limit before instability set in. Brunt and Low tried to apply this result to the existence of large lapse rates near the ground on hot days. Later Jeffreys improved on Rayleigh's results and obtained similar expressions for instability, but he "could not say how far the result could apply to the atmosphere". Hales, applying the theory to the atmosphere, showed that the *form* of the result was not different from that obtained by the previous workers and deduced that only over a limited height, super-adiabatic lapse rates may occur, *i.e.*, the potential temperature cannot decrease with height for any large interval of height.

It may be argued that the top-heaviness due to the difference in the moisture content in different layers may lead to a different form of result and bring about instability. This can be disposed of without great details. The fundamental equations of instability in the thermal problem for a thin layer of air are:

$$d/dt \quad (u, v, w) - \nu\rho \ \Delta \ (u, v, w) = - (\partial/\partial x, \partial/\partial g, \partial/\partial z).p - (o, o, g\rho) \qquad (1)$$

$$d\rho/dt = \rho \ \text{div.} \ (u, v, w) \qquad (2)$$

$$d\theta/dt = k \ \Delta \ \theta \qquad (3)$$

$$\rho = \rho_0 (1 - \alpha\theta), \qquad (4)$$

---

[1] Rayleigh, *Phil. Mag.*, **32**, 529. *Coll. Works*, **6**, 432. Low, *Nature*, **65**, 299. Brunt, *ibid.*, 300. Jeffreys, *Phil. Mag.*, 1926, **2**, 833 and *Proc. Roy. Soc.*, 1928, **118**, 195. Low, *Proc. Roy. Soc.*, 1929, **125**, 180. Jeffreys, *Proc. Camb. Phil. Soc.*, 1931, **26**, 170. Malurkar, *Gerland's Beitr. Geophys.*, 1937, **51**, 270. Hales, *Proc. Roy. Soc.*, **151**, 624. Also Malurkar in the Abstracts Nos. 28, 29, 37 of 1937 of the Physics Section of the Indian Science Congress.

where u, v, w are components or velocity of the fluid, p is the pressure, ρ the density at any point, ν the viscosity, θ the temperature, k the thermal diffusivity, ρ_0 the intitial density and α is a constant. The z-axis is measured vertically upwards and Δ is used as usual for $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$.

The equations (1) and (2) do not explicitly involve temperature; (1) is the general equation of motion in a fluid taking account of viscosity and (2) is the equation of continuity. But equations (3) and (4) depend on temperature. Taylor[2] showed that in eddy diffusion, the moisture content or more accurately the mixing ratio obeyed an equation similar to the equation of heat conductivity. It is also well known that the density of air and the mixing ratio have a linear relation when thin layers are considered. If a thin layer of uniform temperature is considered and r the mixing ratio is taken to decrease uniformly with height to bring about top-heaviness equations (3) and (4) are replaced by similar equations involving mixing ratio

$$dr/dt = k' \Delta r \tag{5}$$

$$\rho = \rho_0 (1 - \alpha' r). \tag{6}$$

The limits of instability can be worked out exactly as in the thermal problem except that the term mixing ratio replaces temperature at each stage of calculation.

The criterion of instability would be, in terms of density, $(\rho_1 - \rho_0)/\rho_0 < \mathrm{K}\, k\nu/gh^3$, where ρ_1 is the density of the top-layer, h the thickness of the layer and K is a constant depending on the boundary conditions. Though investigation on the analogy of Hales to the whole atmosphere, with moisture as variable, has not been carried out, the nature of the equations allow one to be confident that that the criteria of instability brought about by top-heaviness due to temperature gradient and that due to the gradient of mixing ratio are at least to a first approximation analogous.

It follows that between narrow limits, it may be possible to have top-heaviness owing to higher potential temperature at the lower levels or owing to injection of extra moisture in the lower layers. But instability rapidly sets in if the height interval is large. The top-heaviness which can exist in very shallow layers as deduced in the various papers on the basis of stability would not allow instability to set in without external stimulus; or initiation of convection without external stimulus is not likely in such systems. The cause of initial upward motion must, therefore, be sought for elsewhere

[2] Taylor, *Phil. Trans. Roy. Soc.*, **1915, 215**, 1.

than in the general or widespread temperature and humidity distribution that already exists. The possible local causes of upward motion are:

(*a*) Strong *unequal* surface heating—If there was equal heating of the various strata in the very low layers of the atmosphere, the criteria developed previously may perhaps give rise to large lapse rates without creation of instability when thin layers are considered. But when there is unequal heating in any level such isolated stable strata or pockets of air do not form and upward motion is facilitated. In nature, the unequal heating is more likely; due to the fact that large tracts are covered by vegetation and others bare. The rivers, large water surfaces, uneven land or land not covered uniformly by vegetation or even non-uniform distribution of rocks and earth make the surfaces of equal temperature deviate largely from a horizontal position and upward motion can be initiated. The deviation of the isothermal surfaces from the horizontal would generally be great during the afternoons and early evenings. Even at other times, the non-horizontality of the isothermal surfaces brought about by differential cooling of the land and water surfaces may give rise to upward currents. When the top surface of a cloud cools by radiation and sinks, upward motion may indirectly be induced.

(*b*) If the surfaces of equal humidity are not horizontal and the gradient of humidity or mixing ratio sufficient, upward currents can be initiated. The analogy with temperature gradient can profitably be used.

(*c*) At the surface of separation of two air masses large waves may be set up and in portions of the wave, upward motion is possible.

(*d*) Gradient of wind velocity due either to (i) orography, or (ii) juxtaposition of two air masses with very different horizontal velocities. When land rises abruptly, there is an upward component of wind whenever the wind blows against the land. When two air masses meet with very different horizontal velocities the equation of continuity would indicate that large upward motion of air can take place. At a cold front or whenever there is wedge of cold air, the air adjacent to it will be lifted up.

In the large-scale operations of the atmosphere, a mass of air rising due to unequal heating may be considered as an isolated air mass obeying the well-known equation

$$\frac{d^2z}{dt^2} = g\,(\theta_r/\theta_a - 1), \qquad (1)$$

where θ_r is the temperature of the rising mass, θ_a is the temperature of the air immediately surrounding it and z is the vertical height measured upwards. The friction and the dissipative forces have been neglected. The

equation cannot be solved in general. A simple case of an atmosphere with a uniform lapse rate μ can be taken. At the initial level the temperature of the free air may be θ and that of the rising air $\theta + \alpha$. The rising air cools at the dry adiabatic rate λ. At the initial level the rising mass may be taken to have no upward extra velocity imparted to it, *i.e.*, would start from rest. Then

$$\frac{d^2z}{dt^2} = g\,(\alpha - \lambda z + \mu z)/(\theta - \mu z) \tag{8}$$

$$\frac{1}{2}\left(\frac{dz}{dt}\right)^2 = g/\mu^2\,\{(\lambda - \mu)\,\mu z - (\alpha\mu - \lambda\theta + \mu\theta)\,\log\,(1 - \mu z/\theta)\} \tag{9}$$

dz/dt would be zero at $z = 0$ and again at the point given by

$$\mu\,(\lambda - \mu)\,z = (\alpha\mu - \lambda\theta + \theta\,\mu)\,\log\,(1 - \mu z/\theta). \tag{10}$$

As θ is large compared with λ, μ or z the equation can be approximately solved and dz/dt is equal to zero at

$$2\alpha \Big/ \left(\lambda - \mu - \frac{\alpha\mu}{\theta}\right) \tag{11}$$

while $d^2z/dt^2 = 0$ at $\alpha/(\lambda - \mu)$.

The level to which a mass of air rises due to its being lighter than its surroundings at any stage is not limited by the fact that at the terminal position the density must be equal to that of the surrounding air. The acceleration alone is reduced to nothing at the point of hydrostatic equilibrium. The momentum developed by the rising current would be able to carry the mass to a level considerably above the level of hydrostatic equilibrium. When this rising mass, after having overshot the hydrostatic equilibrium level, comes to rest at the hydrodynamic equilibrium level, it would be colder or denser than its immediate surroundings and would descend. Similarly during descent, the mass would go quite well below the level of hydrostatic equilibrium and find itself warmer or lighter than its surroundings. It will rise again and would execute oscillations. The initial amplitude would be small if the rise of potential temperature with height was large as the rising mass has nearly a constant potential temperature. If the increase in potential temperature with height is relatively smaller the amplitude of the oscillations would correspondingly be greater.

In any particular problem, however, the successive amplitudes diminish, perhaps rapidly, due to the dissipative forces like resistance and mixing. For the problem on hand, it is not necessary that oscillations *should take place* but that the rising mass must be able to go above the level of static equilibrium.

In the thermodynamic treatment, the actual mode of rise of air is not very material. And often, the treatment is more or less static. The importance of the extra ascent between the levels of static and dynamic equilibrium is that though a mass of unsaturated air may not reach the stage of condensation before the static level, yet it may attain saturation before the dynamic level of equilibrium is reached. In the above equations it is easily seen that the extra height between the levels of static and dynamic levels is nearly of the same order as that between the initial level and the level of static equilibrium. In other words a mass of air which would have cooled by 10° C. by rising one kilometre to reach its static level of equilibrium may cool nearly 15 to 20° C. before the dynamic level of equilibrium is reached. The difference involved is obvious. The dynamical treatment allows the condensation point to be attained for a rising mass which is much drier than the semi-static treatment. If the condensation is reached before the level of static equilibrium is reached, no special complications arise.

When the rising mass attains its saturation point and condenses, latent heat, which is comparatively large for water vapour, is liberated and it heats the air immediately surrounding the rising mass. This heated air has the impetus to rise due to this extra energy and may in turn initiate further upward motion. The system becomes self-regenerating and, if conditions are favourable, may grow at a continuously accelerated pace to result in a thunderstorm.

If the initial upward movement is due to unequal distribution of humidity and there is sufficient gradient of humidity upwards, arguments similar to the ones above can be used by replacing lighter for warmer and denser for colder. Once the condensation point is reached and the latent heat warmed the surrounding air, the further development would be similar to the upward motion due to extra heat imparted to the rising mass.

When the upward movement is due to horizontal gradient of wind, either due to orography or frontal action, the density of air at the initial place of vertical motion is not lighter than the surrounding air. Hence the upward motion of air due to gradient of wind may be considered as analoguous to the stage described in the previous paragraphs when the lighter air had passed the level of static equillibrium but not yet come to rest, *i.e.*, still possessed upward momentum. If this air reached its condensation point before the level of momentary rest is reached, the liberated latent heat would give the surrounding air impetus for further vertical motion after which the previous arguments may be applied.

In nature the conditions described as of distinct types do not occur individually. More than one condition is operative. The orography may be helped by extra surface heating and bringing in of moisture in the lower levels or relative drying up of higher levels.

Incidentally, it may be mentioned that during the process of condensation and vertical movement, strong horizontal winds would drift away the products of condensation and may inhibit the development of a thunderstorm. Weaker winds at higher levels would help the growth of a thunderstorm. The inversions may also help to conserve or localise the accumulation of energy. Every small addition of heat or moisture in the lower layers can be dissipated away by convection currents. The inversion by preventing these small currents would allow sufficient energy to be accumulated in the lower layers and when the convection is brought into play to counteract the effect of inversion, it may do so with explosive violence.

When a uniform plate is heated from below the convection currents that are set up form isolated upward streams. There is no general upward transference of air over the whole plate. The actual places where these small rising currents are set up probably depend on irregularities on the surface. Even otherwise the points of ascent would perhaps be determined by the physical characteristics of the plate, *e.g.*, the points of ascent would somewhat be similar to the nodes of the Chladni's figures on the plate. The problem in nature, the places of occurrence of heat thunderstorms, may be compared to the patterns of nodes and anti-nodes in a loaded plate with suitable boundary conditions corresponding to the rivers, hills and other items of orography. This analogy was thought out during a conversation with L. P. Cohen and may profitably be followed up.

From a practical point of view, the above discussion leads one to the useful conclusion in the case of heat thunderstorms: if at higher levels fresh air which is relatively cooler or potentially cooler than the one existed before or if at lower layers relatively warmer or potentially warmer and more moist air than that which existed earlier is brought about, the conditions become favourable for thunderstorms. If the convective currents are started these conditions would help to maintain convection and may give rise to thunderstorms.

Summary

The development of a thunderstorm which is essentially a convective phenomenon needs a cause for initial convection and then conditions for its maintenance once started. The possibility of the inherent instability due to potentially colder air superposed on potentially warmer air or the

analogous case of extra injection of moisture in the lower layers is shown to be not applicable in nature and that causes for initial convection must be found elsewhere than in the potential density distribution. Some of the causes are non-horizontality of surfaces of equal temperature and equal humidity; and gradient of wind velocity. It is shown that upward rise of air produced by unequal heating of the ground, does not stop where the rising mass of air attains a density equal to that of the environment (hydrostatic equilibrium), but continues to rise higher till the momentum developed is reduced to zero. The extent of over-shooting is nearly of the same order as the height between the initial level and the level of hydrostatic equilibrium. Once the condensation level is reached, it is well known that the convection will become regenerative due to the evolution of the latent heat of condensation. In the usual treatment of the problem, the ascending parcel of air is expected to condense at or before it reaches the level of hydrostatic equilibrium if it is to develop into a thunderstorm. The dynamical treatment outlined in this paper takes into consideration the overshooting of the parcel of air and thereby allows much drier air to reach condensation and thereafter maintain convection: and can thus account for a larger number of thunderstorms.

THE ACTION OF GRIGNARD REAGENTS ON BENZOPYRONES

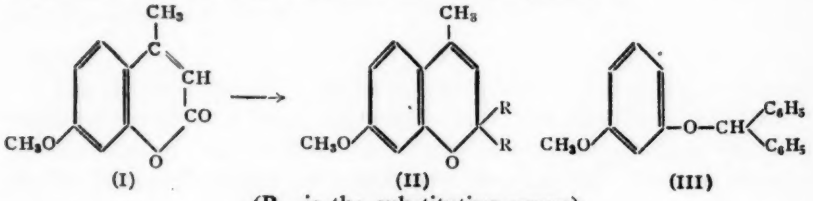
Part I. Preparation of Some Chromenes from 4-Substituted Coumarins

BY A. R. SUKUMARAN KARTHA AND K. N. MENON
(Maharaja's College, Ernakulam)

Received February 17, 1943

THE present investigation was undertaken with the object of synthesising compounds expected to possess insecticidal action similar to that of deguelin. With this object in view the action of grignard reagents on coumarins was taken up. This reaction was employed by Willstätter and co-workers[1] for the synthesis of anthocyanidines. Houben,[2] and Lowenbein, Pongracz and Spiess[3] have also recorded a large number of investigations leading to the formation of substituted chromens and suggested a mechanism for the course of the reaction employing a large excess of the grignard reagent. Heilbron and Hill[4] investigated the action of grignard reagents on substituted coumarins with the object of synthesising flavylium chlorides containing methoxyl and hydroxyl in the 4-position; the latter being expected readily to lose hydrogen chloride and pass into flavones. They obtained only diaryl products and consequently a detailed investigation of coumarins substituted in 3- and 4-positions was initiated. These investigations led them to the definite conclusion that the course of the reaction resulting in the production of either a Δ^2 or Δ^3 chromen is influenced solely by the position of the substituent in the pyran ring.

In this communication we are reporting the condensation of methoxy-methyl umbelliferone with excess of grignard reagents prepared from (*a*) bromobenzene, (*b*) *p*-brom anisol, (*c*) benzyl chloride, (*d*) α-naphthyl bromide, and (*e*) methyl iodide. α- Naphthocoumarin was condensed with magnesium phenyl bromide. All these condensation products are assigned the Δ^3-chromen structure in conformity with the general conclusions arrived at by Heilbron and co-workers, that namely when the 4-position is occupied by a substituent the product formed is the Δ^3-compound.



(I) (II) (III)

(R—is the substituting group)

The 2: 2-diphenyl-4-methyl-7-methoxy-Δ^3-chromen was subjected to alkaline hydrolysis yielding the diphenyl-methyl-ether (III) thereby confirming the Δ^3-structure.

Experimental

The general methods of reaction and processing were the same in all cases and so the details are given only in one case.

2: 2-*Diphenyl*-4-*methyl*-7-*methoxy*-Δ^3-*chromen*.—The grignard reagent prepared from 3 grams (excess) of magnesium and the equivalent amount of bromobenzene was cooled in an ice-bath and treated with 5 grams of methoxy methyl umbelliferon in dry benzene. The reaction mixture was refluxed on the water-bath for 12 hours, decomposed with iced dilute hydrochloric acid and thoroughly extracted with benzene. After removing the benzene the residue was steamed to remove volatile impurities. The residue was extracted with ether, dried and solvent removed, yielding a solid melting at 60–65°. Repeated crystallisation from 95% alcohol yielded clusters of stout flat needles melting at 93°.

(Found: C, 84·1 and H, 6·6. $C_{23}H_{20}O_2$ requires 84·1 and 6·1 respectively.)

2: 2-*Dianisyl*-4-*methyl*-7-*methoxy*-Δ^3-*chromen*.—The crude product obtained from the reaction was a reddish viscous mass and on repeated crystallisation from absolute alcohol yielded needle-like tufts melting at 110°.

(Found: C, 77·4 and H, 6·2. $C_{25}H_{24}O_4$ requires 77·3 and 6·2 respectively.)

2: 2-*Dibenzyl*-4-*methyl*-7-*methoxy*-Δ^3-*chromen*.—The product of the reaction had first of all to be pressed on to a plate to remove the persistently adhering oily impurity and then crystallised from alcohol in rosettes of colourless needles melting at 52°.

(Found: C, 84·2 and H, 6·8. $C_{25}H_{24}O_2$ requires 84·3 and 6·7 respectively.)

2: 2-*Di*-α-*Naphthyl*-4-*methyl*-7-*methoxy*-Δ^3-*chromen*.—The viscous semisolid reaction mass was refluxed with excess of alcohol when an impurity was dissolved out and the product solidified. This processing was repeated with fresh alcohol each time till a fine colourless powder was obtained. Final crystallisation from glacial acetic acid gave a pure product melting at 240–41°.

(Found: C, 86·7 and H, 5·7. $C_{31}H_{24}O_2$ requires 86·9 and 5·6 respectively.)

2:2:4-*Trimethyl*-7-*methoxy*-Δ^3-*chromen*.—The product is a liquid boiling at 158–60°/12 mm.

(Found: C, 76·1 and H, 7·9. $C_{13}H_{16}O_2$ requires 76·5 and 7·8 respectively.)

2:2-*Diphenyl*-4-*methyl*-α-*naphtho*-Δ^3-*chromen*.—The product on crystallisation from a large volume of 95% alcohol yielded yellow prisms melting at 126–27°.

(Found: C, 89·5 and H, 6·3. $C_{26}H_{20}O_2$ requires 89·7 and 5·8 respectively.)

Alkaline hydrolysis of 2:2-*Diphenyl*-4-*methyl*-7-*methoxy*-Δ^3-*chromen*.—2 Grams of the substance was refluxed with 50 c.c. of 50% potassium hydroxide for 60 hours. The solid melted and remained as a viscous liquid on the top of this alkaline solution. After hydrolysis was over the reaction mixture was diluted with 200 c.c. of water, cooled and extracted with ether. The ethereal extracts were united, dried over anhydrous magnesium sulphate and the ether removed. The residue weighed 1·2 grams and solidified to a hard mass. Crystallisation from alcohol yielded needles melting at 105·5°.

(Found: C, 82·3 and H, 6·1. $C_{20}H_{18}O_2$ requires 82·7 and 6·2 respectively.)

Summary

The action of grignard reagents on methoxy methyl umbelliferone and α-naphtho coumarin was investigated to prepare compounds similar to certain naturally occurring benzopyrans.

REFERENCES

1. *Ber.*, 1924, **57**, 1938, 1945.
2. *Ibid.*, 1904, **37**, 489.
3. *Ibid.*, 1924, **57**, 1517.
4. *J. C. S.*, 1927, 2005.

OPACITY CHANGES IN GEL-FORMING MIXTURES DURING SETTING

Part II. Thorium Phosphate, Cerium Phosphate, Thorium Arsenate and Stannic Phosphate Gels

By T. V. Desai and S. Guruswamy

(*Chemical Laboratories, Royal Institute of Science, Bombay*)

Received May 24, 1943

(Communicated by Dr. Mata Prasad, D.Sc., F.I.C., F.A.Sc.)

In a previous communication Prasad and Gogate[1] have reported the results of the measurement of the opacity changes during the formation of thorium molybdate, stannic arsenate, and silicic acid gels with the help of a newly devised apparatus which involves the use of a compensated photocell circuit. The description of the apparatus is given in the author's paper (*loc. cit.*).

In the present investigation the study of the opacity changes has been continued by the same apparatus during the setting of thorium phosphate, cerium phosphate, thorium arsenate and stannic phosphate gels.

Experimental Procedure

The experimental procedure adopted was practically the same as employed by Prasad and Gogate. Varying amounts of the solutions of the two constituents of the gel-forming mixture were taken in two test-tubes and certain amount of distilled water was added so that the total volume of the gelating mixture was 8 c.c. in the case of stannic phosphate and thorium arsenate gels and 9 c.c. in the case of thorium phosphate and cerium phosphate gels. The two test-tubes were corked and kept in the thermostat for about 15 minutes. Then the contents of the test-tubes were mixed and the opacity readings were taken.

The results obtained with each of these gels are given below.

1. Thorium Phosphate Gels

They were prepared by the method of Prasad, Mehta and Parmar.[2] It was found that if a mixture of potassium phosphate and phosphoric acid is employed instead of phosphoric acid alone, the whole system is initially opaque and there is a change in transparency during gelation and the mixture sets into a very transparent gel in a short time. This method of preparing thorium phosphate gel was used and the following solutions were employed:

(A) 6% solution of thorium nitrate (Kahlbaum).
(B) 12% solution of potassium phosphate (Merck).
(C) 1·6 N phosphoric acid.
(D) 0·2 N HCl.

The results obtained during the gelation of thorium phosphate gels are shown by means of curves obtained by plotting the opacity in terms of observed deflections in cm. against time in minutes. The effects of the addition of different amounts of (A), (B) and (C) (D) and of methyl and ethyl alcohols on the opacity changes during the course of gel-formation were investigated.

The effect of thorium nitrate was studied by adding 4 to 6 c.c. of (A) to a mixture containing 0·5 c.c. of (B) and 0·3 c.c. of (C). The effect of phosphoric acid was studied by adding 0·1 to 0·5 c.c. of (C) to 0·5 c.c. of (B) before it was added to 4·5 c.c. of (A). The effect of HCl was studied by adding 0·2 to 0·8 c.c. of (D) to a mixture containing 0·5 c.c. of (B) and

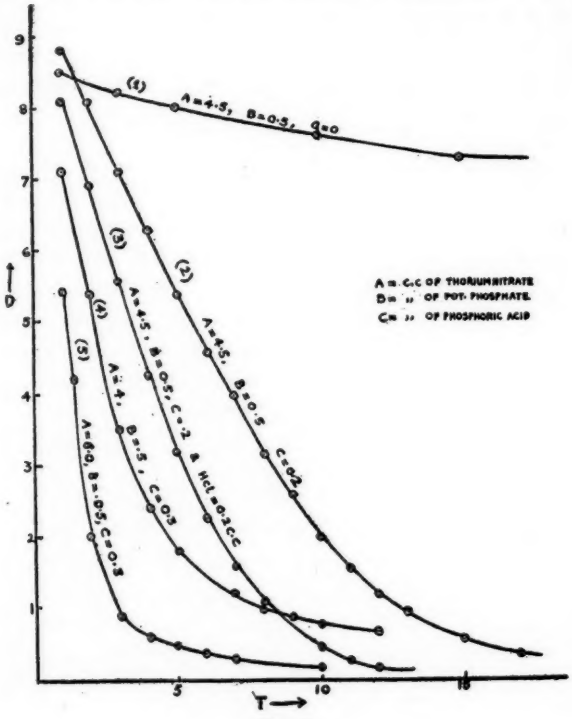


FIG. 1

0·2 c.c. of (C) before it was added to 4·5 c.c. of (A). The effect of ethyl alcohol was studied by adding 0·5 to 1·0 c.c. of ethyl alcohol to a mixture containing 0·5 c.c. of (B) and 0·3 c.c. of (C) before it was added to 4·5 c.c. of (A). The effect of methyl alcohol was studied by adding 0·5 c.c. to 1·5 c.c. of methyl alcohol to a mixture containing 0·5 c.c. of (B) and 0·4 c.c. of (C) before it was added to 4·5 c.c. of (A).

Some results indicating these effects are given in Figs. 1 and 2.

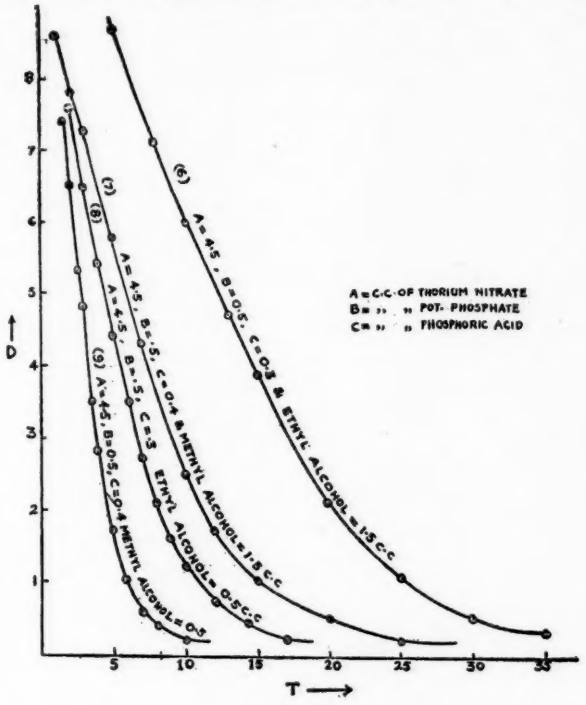


FIG. 2

2. Cerium Phosphate Gels

These gels were prepared by the method of Prasad and Desai.[3] The following solutions were used:

(A) 10% cerium nitrate.

(B) 12% potassium phosphate.

(C) 0·2 N HCl.

The effect of cerium nitrate was studied by addding 4·5 to 7·0 c.c. of (A) to 1·0 c.c. of (B). The effect of potassium phosphate was studied by adding

1·0 to 1·5 c.c. of (B) to 4·5 c.c. of (A). The effect of the addition of HCl was studied by adding 0·5 to 1·0 c.c. of (C) to 1·0 c.c. of (B) before it was added to 4·5 c.c. of (A). The effect of ethyl alcohol was studied by adding 1·0 to 2·0 c.c. of the same to 1·0 c.c. of (B) before it was added to 4·5 c.c. of (A).

Some results indicating these effects are given in Fig. 3.

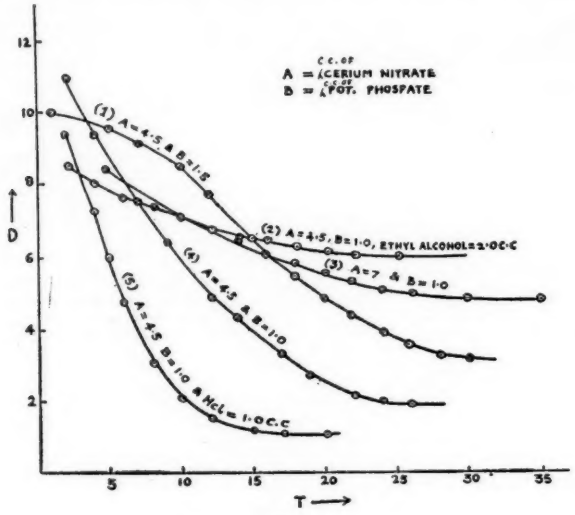


FIG. 3

3. *Thorium Arsenate Gels*

These gels were prepared by the method of Prasad and Desai (*loc. cit.*). The following solutions were used:

(A) 6% thorium nitrate (Kahlbaum).

(B) 10% solution of pyro-arsenic acid (extra pure Merck).

(C) 2 N HCl.

The effect of thorium nitrate was studied by adding 4 to 6 c.c. of (A) to 0·54 c.c. of (B). The effect of pyro-arsenic acid was studied by adding 0·48 to 0·72 c.c. of (B) to 4 c.c. of (A). The effects of HCl, ethyl alcohol, methyl alcohol and glycerine were studied by adding 0·06 to 0·2 c.c. of (C), 0·2 to 0·4 c.c. of ethyl alcohol, 0·1 to 0·3 c.c. of methyl alcohol and 0·06 to 0·1 c.c. of glycerine to 0·54 c.c. of (B) before it was added to 4·0 c.c. of (A).

Some results indicating these effects are given in Fig. 4.

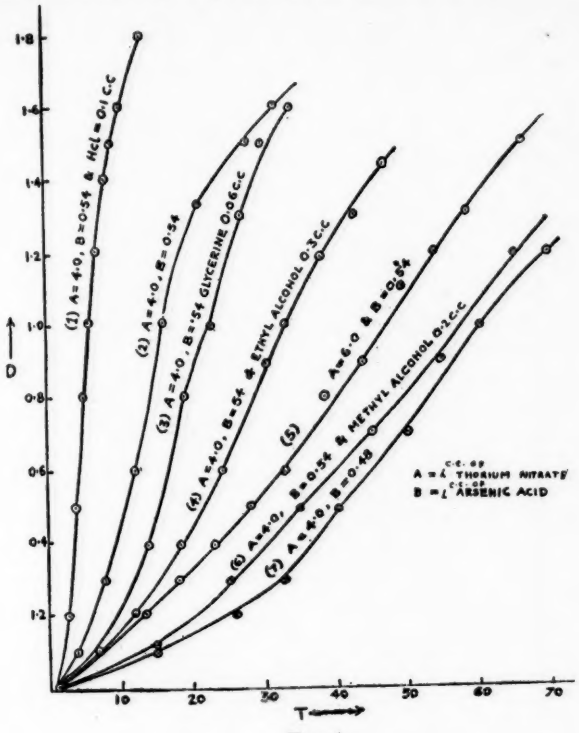


FIG. 4

4. *Stannic Phosphate Gels*

These gels were prepared by the method of Prasad and Desai (*loc. cit.*). The following solutions were used:

(A) 43·82 g. of stannic chloride dissolved in 250 c.c. of distilled water in the presence of 1·0 c.c. of nitric acid to prevent hydrolysis.

(B) 0·2 N phosphoric acid.

(C) 2 N HCl.

The effect of stannic chloride was studied by adding 2·2 to 3·0 c.c. of (A) to 2·4 c.c. of (B). The effect of phosphoric acid was studied by adding 2·4 to 3·0 c.c. of (B) to 3·0 c.c. of (A). The effect of HCl was studied by adding 0·1 to 0·2 c.c. of (C) to 2·4 c.c. of (B), before it was added to 3·0 c.c. of stannic chloride. The effects of methyl, ethyl, propyl alcohols were

studied by adding 1·0 to 2·0 c.c. of methyl alcohol, 1·0 to 2·0 c.c. of ethy alcohol and 1·0 to 3·0 c.c. of propyl alcohol, respectively to 2·4 c.c. of (B) before it was added to 2·4 c.c. of (A).

Some results indicating these results are given in Fig. 5.

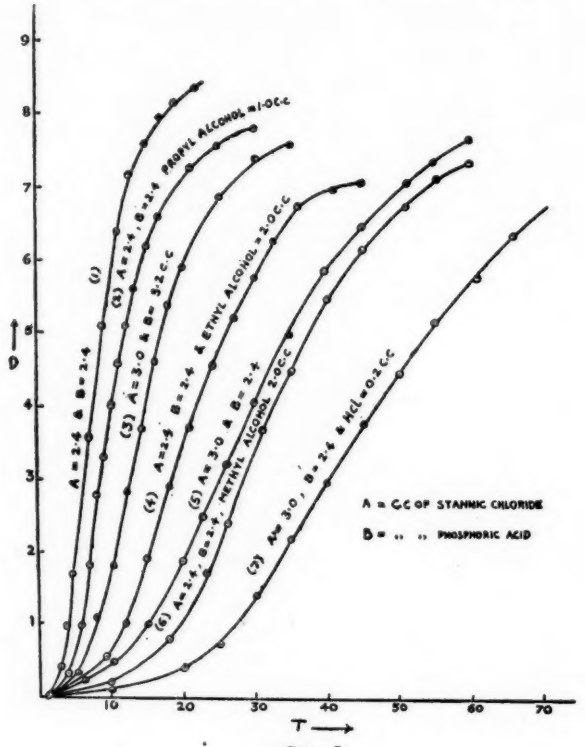


FIG. 5

5. *Discussion of Results*

All the results given above are reproducible and the experimental error is within ± 2 per cent. These results are therefore important as they represent accurately the changes in opacity taking place during the setting of the gels studied in this investigation. The time-deflection curves in all these cases are continuous and thereby indicate that gelation is a continuous phenomenon.

The results obtained in the case of each gel are discussed separately in the following.

1. Thorium Phosphate Gels—

The time-deflection curves (Figs. 1 and 2) show that the gels are opaque in the beginning. The opacity decreases during gel-formation and it reaches a constant value.

It will be noticed from the various curves in Fig. 1 that increasing amounts of thorium nitrate (curves 4 and 5), phosphoric acid (curves 1 and 2) and HCl (curves 2 and 3) in the gel-forming mixture increase the rate of change of opacity and make the gel more and more transparent. It is interesting to note that a small quantity of phosphoric acid is able to make the gel very transparent.

Non-electrolytes exercise a great influence on the course of gel-formation. Increasing amounts of methyl alcohol (curves 6 and 8) and ethyl alcohol (curves 7 and 9, Fig. 2) in the gel-forming mixture decrease the rate of change of opacity. In these cases there are no great changes in the final value of opacity.

In the case of these gels the plot of log d against t (d being the deflection at the time t), was found to be a straight line, showing thereby that $d = ae^{-kt}$.

2. Cerium Phosphate Gels—

These gels, like thorium phosphate gels, are opaque in the beginning and become transparent during setting (Fig. 3).

Increasing amounts of cerium nitrate (curves 3 and 4) and potassium phosphate (curves 1 and 4) decrease the rate of change of opacity and make the gel more and more opaque. However, increasing amounts of HCl increase the rate of opacity and make the gel more and more transparent (curves 4 and 5).

The effect of ethyl alcohol is the same as that of cerium nitrate; the rate of change of opacity is decreased and the gel becomes more and more opaque as the amount of alcohol in the gel increases (curves 2 and 4).

In the case of this gel also, log d plotted against t, was found to be a straight line, so that $d = ae^{-kt}$.

3. Thorium Arsenate Gels—

These gels are clear in the beginning and become opaque during setting as shown by the deflection-time curves (Fig. 4).

Increasing amounts of thorium nitrate (curves 2 and 5) decrease the rate of change of opacity, whereas increasing amounts of pyro-arsenic acid (curves 2 and 7) increase the rate. Increasing amounts of HCl increase

the rate of change of opacity (curves 1 and 2). Non-electrolytes employed are ethyl and methyl alcohols, and glycerine. Curves 2 and 4, 2 and 6, 2 and 3, respectively, show their effects. It will be seen that non-electrolytes decrease the rate of change of opacity.

4. Stannic Phosphate Gels—

The deflection-time curves in Fig. 5 show that the stannic phosphate gels are clear in the beginning and they increase in opacity during gel-formation and reach a constant value.

The rate of change of opacity is decreased by the addition of increasing amounts of stannic chloride to the gel-forming mixture (curves 1 and 5), whereas increasing amounts of phosphoric acid increase the rate of change of opacity (curves 3 and 5).

Increasing amounts of HCl decrease the rate of change of opacity (curves 5 and 7). Curves 1 and 6, 1 and 4, and 1 and 2 represent the effects of the addition of increasing amounts of methyl, ethyl and propyl alcohols to the gel-forming mixture. It will be seen that their addition causes the decrease in the rate of change of opacity of the gel-forming mixture.

One of the factors that causes the change of opacity is the change in the intensity of the scattered light by the gel-forming mixture with time. The intensity of light scattered by a colloid system is given by Lord Rayleigh's equation,[4] which under standard and fixed conditions can be written as

$$I = kV^2 N,$$

where N is the number and V, the volume of the scattering particles. The observed changes in the opacity during gel-formation may be due to changes in these two factors during the setting of the gels.

Changes in the intensity of scattered light which cause changes in opacity may also be brought about by changes in the anisotropy, arrangement and distribution of the micelles in a gel as pointed out by Prasad and Gogate. It is quite probable that changes in the anisotropy, distribution and arrangement of the micelles in the gel taking place with the changes in the amounts of the constituents of the gel-forming mixtures may be responsible, to a great extent, for the rate of change of opacity and also for the final value reached at the completion of the gelation process.

Further work on the changes in the intensity and depolarisation factors of the light scattered by gels during and after gelation is in progress. From the total scattering observed an attempt is being made to separate the

scattering due to size, number and anisotropy and to study their changes during gelation.

The authors feel grateful to Dr. Mata Prasad, D.Sc., F.I.C., for suggesting the problem and for the guidance throughout the progress of this work.

6. *Summary*

The opacity changes during the formation of gels of thorium phosphate, cerium phosphate, thorium arsenate and stannic phosphate have been investigated. Opacity-time curves, in the case of thorium and cerium phosphate gels, are exponential in character.

The changes in the opacity with time of the gels formed from different amounts of the constituents of the gel-forming mixture and the effects of HCl and non-electrolytes on the course of gel-formation have been investigated. In general non-electrolytes decrease the rate of change of opacity, while HCl increases the same.

The final values of opacity are not the same in all these cases but they vary with the concentration of the constituents of the gel-forming mixture. It has been suggested that the changes in the rate of changes of opacity and the final value of opacity may be due to the changes in the number, size, anisotropy, distribution and arrangement of the micelles taking place under the different conditions of the gel-formation.

REFERENCES

1. *Proc. Ind. Acad. Sci.*, 1943, **17**, 161.
2. *J. Indian Chem. Soc.*, 1936, **13**, 69-71.
3. *J. Univ. Bom.*, 1938–39, **7**, 148.
4. *Phil. Mag.*, 1899, **47**, 375.

EXCITATION PROCESSES IN THE NIGHT SKY AND THE AURORA

By Ta-You Wu

(Department of Physics, National University of Peking, and Institute of Astronomy, Academia Sinica, Kun-ming, China)

Received July 2, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction

Our knowledge concerning the conditions prevailing in the upper atmosphere of the earth comes mainly from the following two sources: (1) From the behaviour of the ionized layers towards radio waves and the magnetic variations, it is possible to make certain estimates of the concentrations of electrons, heavy ions and neutral particles in the different layers. In the present work, we shall not be concerned with the various aspects of these problems. Suffice it to summarize the main results as follows[1]:

	Electron density		Heavy ion density	Collision freq. of electron	Concentration of neutral particles
	Day	Night			
F layer 200–300 km. ..	3×10^5/c.c.	2×10^5/c.c.	10^5–10^6/c.c.	6×10^3/sec.	10^{12}/c.c.
E layer 100 km. ..	$1{\cdot}5\times10^5$/c.c.	8×10^3/c.c.	10^3/c.c.	2×10^6/sec.	3×10^{13}/c.c.

The ionization and the dissociation of the atoms and molecules are due to the ultraviolet radiations from the sun. The rather slow falling off of the electron density after sunset and the much higher concentration of heavy ions than that of electrons, are due to the small probability of recombination between electrons and positive ions and the much more frequent occurrence of attachment process of electrons to neutral atoms and molecules, the former process taking place at the rate of about 10^{-5} per second and the latter about 1 per second at the pressure of the E layer.

(2) From the analysis of the spectra of the night sky and the aurora, it is found that in both cases the radiations consist of the forbidden lines of

[1] *Cf.* H. S. W. Massey, *Negative Ions*, 1938, Cambridge Univ. Press (1938), pp. 89–100. Later results are unfortunately not available to the writer, but they would not affect the discussions in the following.

[OI], the various band systems of N_2 and N_2^+, some weak bands of O_2 and H_2O and some lines or bands of uncertain origin. There is a great difference, however, between the spectrum of the night sky and that of the aurora borealis, namely, the negative bands of N_2^+ are very strong in the latter but very weak in the former, while the Vegard-Kaplan bands of N_2 are very strong in the former but rather weak in the latter. In each individual band system, certain bands in certain sequences are particularly enhanced. Evidently a clear understanding of the excitation mechanisms of these radiations will contribute greatly to our knowledge of the conditions in the upper atmosphere of the earth. For convenience of the discussion, we shall summarize the main features of the spectra of the night sky and the aurora as follows[2]:

(*a*) *The forbidden lines of* [*OI*].—The green line at 5577 A is by far the most intense line in the spectrum of the night sky and is also very intense in the aurora. The red lines at 6300 and 6364 A are inferior in intensity in both cases, but are still fairly strong compared with the other bands in each spectrum. In the night sky, the green line increases very slowly in intensity and reaches a maximum towards midnight after which it decreases slowly again.[3,4] The red lines on the other hand have the greatest intensity immediately after sunset and fall off gradually in the night.[4] In the sunlit aurora, the red lines are found to be greatly enhanced relative to the green one.[5]

(*b*) *First negative bands of* N_2^+.—In the aurora spectrum, the following negative bands of N_2^+ are very intense[3]:

4708 A ($v'=0\to v''=2$),	4278 A ($v'=0\to v''=1$),	3914 A ($v'=0\to v''=0$).
4648 (1→ 3),	4236 (1→ 2),	
	4199 (2→ 3),	

The 4708, 4278 and 3914 bands have comparable or even greater intensities than the green 5577 line in the ordinary aurora, and become very much more intense than the latter in sunlit aurora.[2,4] In the night sky, perhaps only the 3914 band can be identified with certainty.[4]

(*c*) *Vegard-Kaplan bands of* N_2.—In the night sky spectrum, the radiations next in intensity to the forbidden lines of [OI] are the Vegard-Kaplan

---

[2] For a summary of the facts concerning the spectra of the aurora and the night sky, see, respectively, E. W. Hewson, *Rev. Modern Physics*, 1937, **9**, 403; and G. Dejardin, *ibid.*, 1936, **8**, 1, and references given there.

[3] *Cf.* G. Dejardin, *loc. cit.*

[4] C. T. Elvey, P. Swings and W. Linke, *Astrophys. Jour.*, 1941, **93**, 337.

[5] L. Vegard and E. Tonsberg, *Nature*, 1936, **137**, 778.

bands of N_2. The bands observed by Sommer, Cabannes[3] and Elvey, Swings and Linke[4] are summarized in Table I.

TABLE I

Vegard-Kaplan Bands in the Night Sky

	v''	10	11	12	13	14	15	16	17	18
v'										
0		3598	3889	4220	4603	5062				
1		3425	3707	3984	4316	4719				
2			3501	3787	4073	4420	4827	5324		
3				3582	3855	4174	4543	4962		
4					3664	3949	4270	4650		
5						3742	4048	4379	4768	
6							3834	4144	4493	
7					3211?	3424?		3936	4259	4616

Of these, the 4073, 4171, 4270, 4420, 4543 and 4827 bands from the levels $v' = 2$, 3, 4 are the most intense. In the aurora spectrum, some 10 stronger ones of these bands have also been identified, although they are in general very weak.[6]

(*d*) *First positive bands of* N_2.—In the aurora spectrum, the bands observed by Vegard at 6323 and 7880 A have been identified with the $v' = 10 \rightarrow v'' = 7$ and $v' = 7 \rightarrow v'' = 6$ transitions respectively. In the spectrum of the night sky, a number of first positive bands has been found, the more intense ones being those from the vibrational levels $v' = 7$ and 15 according to Cabannes.[3] More recently, Elvey, Swings and Linke have identified from their own and Babcock's observations the following bands (4→1), (7→4), (8→4), (8→5), (9→6), (10→4), (10→5), (11→5), (11→8) (12→7), (12→8), (13→8), (13→9), (14→9), (15→11), (16→12). These are weak compared with the Vegard-Kaplan bands.

(*e*) *Second positive bands of* N_2.—In the aurora, the sequences $v'' - v' = -1$, 0, 1, 2, 3, 4, with v' from 0 to 5 and 6, are observed. They are weak compared with the negative bands of N_2^+. In the night sky, the bands of the second positive system are very weak. Cabannes found the bands 4574 A ($v' = 1 \rightarrow v'' = 6$), 4059 A ($v' = 0 \rightarrow v'' = 3$), 3998 A ($v' = 1 \rightarrow v'' = 4$). On the other hand, these bands do not appear in Elvey, Swings and Linke's spectrograms. These authors found instead only the 3159 (1→0) and the 3371 (0→0) bands; even then the identifications are not certain since each

[6] *Cf.* J. Kaplan, *Phys. Rev.*, 1938, **54**, 198, and reference given to the works of Vegard.

of these bands can be equally well ascribed to other transitions in other band systems.

(*f*) *Lyman-Birge-Hopfield bands of* N_2.—The existence of bands of this system, especially those from $v' = 0$ to $v'' = 19 - 23$, has recently been made plausible by the observations and identifications of Elvey, Swings and Linke.[4]

(*g*) *Atmospheric bands of* O_2.—The observations and analysis of Cabannes seem to suggest the existence of the A, B, α, α', α'', bands of O_2 at $0{\cdot}76\,\mu$, $0{\cdot}69\,\mu$, $0{\cdot}63\,\mu$, $0{\cdot}58\,\mu$, $0{\cdot}54\,\mu$, corresponding to the transitions $0\rightarrow0$, $1\rightarrow0$, $2\rightarrow0$, $3\rightarrow0$, $4\rightarrow0$ respectively.[3] On the other hand, from Babcock's and their own observations, Elvey *et al.* concluded that probably only the α' band is present in the spectrum of the night sky.[4]

(*h*) *Schumann-Runge bands of* O_2.—Elvey, Swings and Linke showed from their own observations, and Kaplan from those of Gauzit, that the positions of certain ultraviolet bands in the night sky agree quite well with the transitions $v' = 0$, $1\rightarrow v'' = 12 - 18$, in the Schumann-Runge system and suggested their probable presence.

(*i*) *The yellow lines of Na.*—The yellow lines of Na have been observed by Bernard, Cabannes and others at 5893 A in the spectrum of the night sky.[7] They are not observed in the aurora.

(*j*) *Water vapour bands.*—The observations and analysis of Cabannes[3] seem to suggest strongly the presence of the water vapour bands at $0{\cdot}59\,\mu$, $0{\cdot}65\,\mu$, $0{\cdot}698\,\mu$, and $0{\cdot}72\,\mu$. On the other hand, from their own and Babcock's observations, Elvey, Swing and Linke concluded that probably only the $0{\cdot}65\,\mu$ band is present in the spectrum of the night sky and regarded the problem of water vapour bands in the night sky as unsettled.

In addition to these, there are some weaker lines or bands of uncertain origin in both the spectrum of the night sky and that of the aurora. But undoubtedly the above-mentioned radiations are the most important features in both cases.

To explain the cause of the auroræ, their shapes and spectral characteristics, many theories have been proposed. A common feature of the more successful ones is that the emission of radiations of the aurora is excited by swift particles which may be directly ejected from the sun, or may be secondary particles resulting from these corpuscular rays or from ionization of the uppermost atmosphere by sudden outbursts of ultraviolet

---

R. Bernard, *Astrophys. Jour.*, 1939, **89**, 133; J. Cabannes, J. Dufay and J. Gauzit, *ibid.*, 1939, **88**, 164, and references to earlier papers given in these papers.

radiations from the sun. These theories, while successful in furnishing a source of energy for excitation and explaining the forms of the auroræ, and their concentration near the poles, cannot account for the selective nature of the excitations of the various radiations, and in particular, for the enhancement of certain bands in a system. Corpuscular rays, whatever they may be, must be expected to have a certain spread in energy; and as the excitation functions of atomic and molecular transitions by electron impact do not possess sharp maxima in general, one would expect more or less non-descript rather than the highly selective excitations observed. Also the complete absence of radiations corresponding to the allowed transitions in the atoms of N, O, He and H would be difficult to understand,[8] as the difference between the excitation potentials of these atoms and those of the observed lines and bands would be small compared with the energies available in the corpuscular rays. Hence it appears that while these theories may be correct in dealing with the large-scale features, the corpuscular rays cannot be solely responsible for the excitations of the radiations in the aurora and in the night sky.

Towards the understanding of the nature of the mechanism in the excitation processes in the upper atmosphere, considerable progress on the experimental side has been made by Kaplan by reproducing very closely the various spectral characteristics of the aurora and the night sky by running electrical discharges and afterglows under special conditions in the laboratory.[9] Thus he found that it is possible to produce the green [OI] line, the Vegard-Kaplan bands and other bands of N_2 and N_2^+ in various relative intensities by varying the conditions of the discharge. The production of the Vegard-Kaplan bands not only shows that the metastable $N_2(A^3\Sigma)$ molecules are present but suggests that they may play an important rôle in the excitation of the other bands. In fact it is possible to explain the enhancement of the bands from $v' = 6, 7$ and $v' = 10, 11$ in the first positive system of N_2 in an afterglow in active nitrogen as the result of collisions of the second kind Q_{10} and Q_9 in Table II. While these

[8] We believe that the absence of the He and H lines in the aurora and the night sky is no argument against the presence of He and H in the upper atmosphere, but means that the excitation condition there is not adequate for the production of the lines of He and H as well as those of N and O. In fact, there is some indication, although uncertain, for the presence of two NH bands 3371 A (0→0) and 3360 A (1→1) in the night sky, according to Kaplan, *Phys. Rev.*, 1939, **55**, 593, and Elvey, Swings and Linke, *loc. cit.* If these identifications are correct, they would indicate the presence of atomic H in the upper atmosphere, which forms NH on combining with the N atoms.

[9] Kaplan's experiments are reported in various issues of the *Physical Review* and the *Nature* from 1928 to the present day.

experiments are exceedingly valuable in throwing considerable light on the problem, one cannot immediately identify the conditions in the upper atmosphere with those in the discharge tubes. In the latter, excitations by electron impact play a rôle that cannot be ignored, while in the upper atmosphere excitations by electron impact become impotent on account of the low energies of the free electrons, unless one invokes high energy electrons in corpuscular rays, in which case one introduces the difficulty with the selective excitations discussed above. The considerable difference in pressure in the discharge tube and in the upper atmosphere is another factor that must be reckoned with, since the question whether a forbidden transition radiates or not depends on the frequency of quenching collisions, which is in turn determined by the concentration of the appropriate colliding particles. Even the walls of the discharge tube constitute a great difference from the atmosphere, since they furnish the most efficient third-body for the formation of metastable molecules on recombinations between the atoms, while a three-body collision becomes a rare event in the upper atmosphere on account of the low pressure there.

On the theoretical side, many theories have been proposed for the excitation mechanisms in the upper atmosphere, among which the one due to Chapman seems to be most favoured by many authors.[10] According to it, the source of energy of the radiations in the night sky is the energy of dissociation of the oxygen molecules stored up during the day, and the radiations of the O atom and the N_2 molecule are excited when two O atoms recombine in their neighbourhood in a three-body collision. We shall show in the following that the frequency of occurrence of such three-body collisions is entirely much too low to account for the observed intensities of the various radiations and that the theory is inadequate in explaining the diurnal intensity variations of the most prominent radiations in the night sky.[16] It is proposed to show that the main spectral features, especially of the night sky, can be satisfactorily understood on the view that the key processes are the formation of the metastable molecules of oxygen and nitrogen by radiative recombinations between the atoms generated during the day, and the excitation processes are then the various collisions of the second kind, of the resonance type, between the metastable molecules and atoms. It is important that any suggested mechanisms be not judged on energetic considerations alone; it is necessary to pay a closer attention to the

[10] S. Chapman, *Phil. Mag.*, 1937, **23**, 657. Most unfortunately this journal is not available either in Kun-ming or in Chungking; but from another paper by Chapman, *Astrophys. Jour.*, 1939, **90**, 309, and a paper by Cabannes, *Comptes Rendus*, 1939, **208**, 1770, it is gathered that only dissociation of O_2 and three-body recombinations are considered.

rates at which the various processes might take place in the upper atmosphere and to see if they may account for the observed intensities of the radiations. For this a closer discussion of the probabilities of the various processes is necessary.

Theory

We shall start with an atmosphere that is composed mainly of N_2, a smaller amount of O_2, some rare gases and some water vapour, and assume that as the result of dissociation and ionization of the N_2 and O_2 molecules by the ultraviolet solar radiations, there are also present N and O atoms, N_2^+ and O_2^+ ions as well as N^+ and O^+ ions. These ions, the electrons and the negative ions formed by the attachment of electrons to neutral atoms and molecules do not play any direct rôle in the excitation processes in the theory and hence will be ignored in the following. The primary processes are:

$$N_2(X\,^1\Sigma) + h\nu\,(\lambda < 1000\text{ A}) \rightarrow 2\,N\,(^2P), \tag{1}$$

$$N_2(X\,^1\Sigma) + h\nu\,(\lambda < 1200\text{ A}) \rightarrow N\,(^2D) + N\,(^2P), \tag{2}$$

$$O_2(X\,^3\Sigma) + h\nu\,(\lambda < 1750\text{ A}) \rightarrow O\,(^3P) + O\,(^1D), \tag{3}$$

and to a less extent and in the lower atmosphere,

$$O_2(X\,^3\Sigma) + h\nu\,(\lambda < 2400\text{ A}) \rightarrow 2\,O\,(^3P), \tag{4}$$

$$O_3 + h\nu\,(\lambda < 2700\text{ A}) \rightarrow O_2(X^3\Sigma) + O\,(^1D). \tag{5}$$

Positive ions may be produced by the photo-ionization of the N_2 and O_2 molecules and the atoms, by solar radiations of very short wave-length; but it is also possible that the metastable $N_2(A\,^3\Sigma)$ and $O_2(C\,^3\Sigma)$ formed from the N and the O atoms by the processes, Q_1, Q_3, Q_2, Q_4 in Table II contribute greatly to the ionization by absorption of ultraviolet radiations of longer wave-length and hence of greater abundance in the solar radiations.

$$N_2(A\,^3\Sigma) + h\nu \rightarrow 2\,N, \tag{6}$$

$$N_2(A\,^3\Sigma) + h\nu \rightarrow N_2^+(X\,^2\Sigma) + e, \tag{7}$$

$$O_2(C\,^3\Sigma) + h\nu \rightarrow 2\,O, \tag{8}$$

$$O_2(C\,^3\Sigma) + h\nu \rightarrow O_2^+(X^3\Pi) + e. \tag{9}$$

The ionization potentials in (7) and (9) are 9·7 and 7·5 volts respectively compared with the 13·6 and 14·5 volts respectively for the O and N atoms. It is not necessary to exclude the possibility that some dissociation and ionization are effected by agents other than ultraviolet radiations; but as we shall immediately see, on account of the low probabilities for either the radiative or the three-body recombination, the atoms produced in the day by the processes (1), (2), (3), (6) and (8) will disappear slowly enough to account for the rôle they are assumed to play in the night sky. In fact,

for this purpose alone, it is not necessary to invoke the action of agents other than the solar radiations.

On the assumption that there are present in the upper atmosphere the atoms and molecules of N and O but no radiations to remove the metastable $N_2(A^3\Sigma)$ and $O_2(C^3\Sigma)$, as it is the case after sunset, the various processes in Table II are possible. In the following we shall assess their plausibilities. The actual contribution of a given process depends of course, besides on the intrinsic probability of the process, also on the concentrations of the particles involved.

Of these processes, Q_6, Q_7, Q_7', Q_7'', Q_8, Q_9, Q_9', Q_9'', Q_{10}, Q_{10}', Q_{11}, Q_{12}, Q_{12}', Q_{13}, Q_{14}, Q_{15}, Q_{16}, Q_{17} are collisions of the second kind in which the energy of electronic excitation of one particle is transferred into the energy of electronic and vibrational excitation of a molecule. In these cases, the resonance is very close since the vibrational levels are only 1/5 to 1/4 of a volt apart. In Table II the vibrational level which is excited with the

TABLE II

Excitation Processes in the Upper Atmosphere

Notation	Process	Radiation excited
Q_1	$N(^4S) + N(^4S) + X \rightarrow X + N_2(A^3\Sigma)$, v up to 7	Vegard-Kaplan
Q_2	$O(^3P) + O(^3P) + X \rightarrow X + O_2(C^3\Sigma)$,	Herzberg bands
Q_3	$N(^4S) + N(^4S) \rightarrow N_2(A^3\Sigma) + h\nu$	Vegard-Kaplan
Q_4	$O(^3P) + O(^3P) \rightarrow O_2(C^3\Sigma) + h\nu$ [volt	Herzberg bands
Q_5	$O_2(C^3\Sigma) + O_2(C^3\Sigma) \rightarrow O_2(X^3\Sigma) + O(^3P) + O(^1S) + 0{\cdot}12$	Green [OI]
Q_5'	$\rightarrow$ " $+ 2\,O(^1D) + 0{\cdot}37$ volt	Red [OI]
Q_6	$2N_2(A^3\Sigma) \rightarrow N_2(X^1\Sigma) + N_2(C^3\Pi)$, v up to 5	2nd positive
Q_6'	" $\rightarrow$ " $+ 2N(^2D) + 0{\cdot}1$ volt	
Q_6''	" $\rightarrow$ " $+ N(^4S) + N(^2P) + 1{\cdot}3$ volt	
Q_7	$N_2(A^3\Sigma) + O(^1S) \rightarrow O(^3P) + N_2(B^3\Pi)$, $v = 15$	1st positive
Q_7'	" " $\rightarrow$ " $+ N_2(a^1\Pi)$, $v = 9$	Lyman-Birge-Hopfield
Q_7''	" " $\rightarrow O(^1D) + N_2(B^3\Pi)$, $v = 5$	1st positive
Q_8	$N_2(A^3\Sigma) + O(^1D) \rightarrow O(^3P) + N_2(B^3\Pi)$, $v = 3, 4$	" "
Q_9	$N_2(A^3\Sigma) + N(^2P) \rightarrow N(^4S) + N_2(B^3\Pi)$, $v = 11$	" "
Q_9'	" " $\rightarrow$ " $+ N_2(a^1\Pi)$, $v = 6$	Lyman-Birge-Hopfield
Q_9''	" " $\rightarrow N(^2D) + N_2(B^3\Pi)$, $v = 0$	1st positive
Q_{10}	$N_2(A^3\Sigma) + N(^2D) \rightarrow N(^4S) + N_2(B^3\Pi)$, $v = 6$	" "
Q_{10}'	" " $\rightarrow$ " $+ N_2(a^1\Pi)$, $v = 0$	Lyman-Birge-Hopfield
Q_{11}	$N_2(A^3\Sigma) + O_2(X^3\Sigma) \rightarrow N_2(X^1\Sigma) + O_2(B^3\Sigma)$, $v = 0$	Schumann-Runge
Q_{12}	$N_2(A^3\Sigma)' + O_2(C^3\Sigma) \rightarrow O_2(X^3\Sigma) + N_2(C^3\Pi)$, $v = 0$	2nd positive
Q_{12}'	" " $\rightarrow$ " $+ N_2(B^3\Pi)$, $v = 20$	1st positive
Q_{13}	$N_2(A^3\Sigma) + N_2^+(X^2\Sigma) \rightarrow N_2(X^1\Sigma) + N_2^+(B^2\Sigma)$, $v = 11$	1st negative
Q_{14}	$N_2^+(X^2\Sigma) + N(^2P) \rightarrow N(^4S) + N_2^+(B^2\Sigma)$, $v = 1$	" "
Q_{15}	$N_2^+(X^2\Sigma) + O(^1S) \rightarrow O(^3P) + N_2^+(B^2\Sigma)$, $v = 3$	" "
Q_{16}	$O_2(X^3\Sigma) + O(^1D) \rightarrow O(^3P) + O_2(A^1\Sigma)$, $v = 2$	A, B, a bands of O_2
Q_{17}	$O_2(X^3\Sigma) + N(^2D) \rightarrow N(^4S) + O_2(A^1\Sigma)$, $v = 4$	α', α'' bands of O_2
Q_{18}	$O(^3P) + N(^2D) \rightarrow O(^1D) + N(^4S) + 0{\cdot}41$ volt	Red [OI]
Q_{19}	$O(^1D) + N(^2D) \rightarrow O(^1S) + N(^4S) + 0{\cdot}16$ volt	Green [OI]
Q_{20}	$Na(^2S) + N\,^2D) \rightarrow Na(^2P) + N(^4S) + 0{\cdot}27$ volt	Yellow lines Na
Q_{21}	$Na(^2S) + O(^1S) \rightarrow Na(^2P) + O(^1D) + 0{\cdot}11$ volt	" " "
Q_{22}	$Na(^2S) + O(^1D) \rightarrow Na(^2P) + O(^3P) + 0{\cdot}14$ volt	" " "
Q_{23}	$N_2(X^1\Sigma')' + H_2O \rightarrow N_2(X^1\Sigma') + H_2O'$	Water vapour bands

closest resonance is given. The cross-sections of the processes are, however, not solely determined by energy considerations alone. A theoretical evaluation of the cross-sections of such processes is very difficult, as they depend on the coupling between the electronic and the nuclear motions of the molecule. Some rough idea about the order of magnitude of the probabilities of such processes may be obtained from the experiments of Zemansky in which the cross-sections for the de-excitation of Hg $^3P_1 \rightarrow {}^3P_0$ by energy transfer to the vibrational motion of a colliding molecule are found to be of the order of the gas kinetic values.[11] The processes concerned here involve also the excitation of electronic states; their cross-sections may be smaller than the gas kinetic values when the spin rule is violated, but may be of the same order as the latter when the spin rule is satisfied. In the latter category we have Q_7', Q_7'', Q_9', Q_9'', Q_{10}', Q_{12}, Q_{12}', Q_{16}, Q_{17}.

The processes Q_{18} to Q_{22} involve the transfer of purely electronic energies and hence may have very large cross-sections for very close resonance. Their exact values are not known, but it is probable that they lie between 10^{-2} and 10^4 times the gas kinetic values when the spin rule is satisfied and have small values when it is not.[12] Thus of the three processes Q_{20}, Q_{21}, Q_{22} for the excitation of the yellow lines of Na, Q_{21} is by far the most probable both because of the small energy discrepancy and the spin rule.

The processes Q_5, Q_5', Q_6', Q_6'' represent the dissociation of a molecule on collision with another, the energy being furnished, not by the kinetic energy of relative motion, but by the energies of excitation of both molecules. There is involved a transfer of electronic energy to the kinetic energy of the resulting particles and for this reason the cross-sections will be large only when there is very close resonance, *i.e.*, when the amount of energy to be transformed into the kinetic energy of the heavy particles is small. Thus the cross-section of Q_5 may be expected to be very large compared with the others since the spin rule is satisfied and the energy discrepancy is small.

Consider next the radiative processes such as Q_4. If the final state can combine with the quasi-state formed by the close approach of the two atoms

---

[11] Zemansky, *Phys. Rev.*, 1930, **36**, 919.

[12] For processes involving the transfer of electron and electronic energy, reference may be made to the experimental work of Manley and Duffendack, *Phys. Rev.*, 1935, **47**, 56, and of Duffendack and Gran, *ibid.*, 1937, **51**, 804. These show that the cross-section of a process in which a neutral atom is simultaneously ionized and excited on collision with a positive atomic ion may be as large as $10^4 - 10^5$ times the gas kinetic value when the resonance is close. For processes involving the transfer of electronic energy alone, there is the theoretical work of Kallmann and London, *Zeits. f. phys. Chem.*, 1929, **B 2**, 220, but no experimental work seems available. It is probable that the cross-sections are of the same order as those above.

by dipole transitions, the cross-sections may be estimated on general considerations at 10^{-7}—10^{-5} times the gas kinetic values for slow atoms,[13] and are hence small compared with those of the resonance collisions of the second kind. That they cannot be omitted from our considerations is due to the fact that they are still the chief mechanisms for the recombination of atoms in the upper atmosphere and are the source of energy of the excitation and radiation processes in the night sky, and possibly to a certain extent in the aurora. The other recombination processes, namely, three-body collisions such as Q_1, have even smaller probabilities at the low pressure of the upper atmosphere. The probability of a three-body process may be expressed in terms of a cross-section for unit concentration of the third body, namely, $q \simeq \pi\ r^2 \cdot r/\lambda$, where r is the atomic dimension and λ is the mean free path of the recombining particles for unit concentration of the third body.[13a] Obviously λ depends on the cross-section of the energy transfer from the recombining particles to the third body. Assuming, for the optimum case, that there is resonance in this transfer so that the cross-section may be as large as 10^3 times the gas kinetic value, one obtains for λ a value 10^{13} cms. and then $q \simeq 10^{-37}$ cm.[5] Hence for the three-body collisions to be as frequent as the radiative recombinations, the concentration of the third body must be as high as 10^{15} per c.c. or greater. This value is about 10^2 to 10^3 times greater than the concentration at the E layer. Hence in the upper atmosphere, radiative recombinations are far more important than three-body processes, although in the lower atmosphere and in all laboratory experiments the reverse is the case.

Finally, in order that excitation collisions between metastable atoms and molecules be of any importance, it is necessary that de-excitations of the metastables by collisions with atoms and molecules be negligible. Now the latter process involves the transfer of electronic energy to the kinetic energies of the heavy particles (atoms and molecules); its probability can be calculated by means of the principle of detailed balancing from the probability of a process in which the electronic state of an atom or a molecule is excited by heavy particles in a collision of the first kind. As shown by Massey and Smith,[14] the probabilities of excitation of the $2\ ^1P$ state of He by protons are extremely small for proton energies below 400 volts. On general considerations, one would expect the probabilities of excitation of metastable states

---

[13] *Cf.* Massey, *Negative Ions*, pp. 32–36; 78–79. As the number of molecular states arising from two atoms in given atomic states is very large, for a given state of the molecule it is in general possible to find a quasi-state having the correct symmetry properties so as to combine with the state by dipole transitions.

[13a] J. J. Thomson, *Phil. Mag.*, 1924, **47**, 337; *cf.* Massey, *Negative Ions*, pp. 38–39; 79–80.

[14] Massey and R. A. Smith, *Proc. Roy. Soc.*, 1933, **A 142**, 142.

(*i.e.*, optically forbidden transitions) by heavy particles to be even smaller. The principle of detailed balancing then requires that the probabilities of the reverse processes, namely, the de-excitation of metastable states by heavy particles, be also extremely small, especially for the kinetic energies of atoms and molecules with which we are concerned in the upper atmosphere. It is because of these extremely low probabilities of de-excitations by atoms and molecules and the comparatively high concentrations of the metastables that the collision processes in Table II, which are mostly of the resonance type, assume relatively great importance in the upper atmosphere.

From the above discussions, however, it would appear that nothing quantitative can be said concerning the probabilities of the various processes in Table II. Fortunately, most of our arguments in the following do not depend very critically on the exact values of these probabilities, although a more exact knowledge about them will enable one to make closer estimates of the concentrations of the various atoms and molecules and is hence greatly to be desired.

Consider now the various radiations in the spectra of the night sky and of the aurora in the light of the processes in Table II. In the following we shall denote the concentration of the atom, say, O (^{1}S), by [O ^{1}S], and the number of collisions, say, O (^{1}D) + N (^{2}D)→O (^{1}S) + N (^{4}S), in unit volume per second by Q_{19} [O ^{1}D] [N ^{2}D] so that Q_{19} represents the cross-section of the process multiplied by the relative velocity of the colliding particles. For the three-body processes, q represents the cross-section for unit concentration of the third body.

(*A*) *Green* [*OI*] *line*: $^1S \rightarrow {}^1D$

Since the green [OI] line is the most prominent line in both the spectra of the night sky and of the aurora, any theory must not fail to provide a satisfactory mechanism for the excitation of the line. From the earliest experiments of Kaplan in which the green line was excited in an afterglow in active nitrogen containing a small amount of oxygen, the suggestion was made that the ^{1}S state is excited from the normal state ^{3}P by the metastable atom N (^{2}P).[15] This explanation is now untenable since the energy available in N (P) is far short of being able to effect this excitation. Chapman and later Cabannes suggested that the various radiations of the night sky are excited by the recombinations between the oxygen atoms in the neighbourhood of another atom or molecule.[10] For example, the green [OI] line is thought to be due to the process

$$O\,(^3P) + O\,(^3P) + O\,(^3P) \rightarrow O_2\,(X\,{}^3\Sigma) + O\,(^1S) + 0{\cdot}92 \text{ volt.}$$

[5] J. Kaplan, *Phys. Rev.*, 1929, **33**, 154.

It can be shown, however, that even on making the most optimum assumption about the probability of the three-body process, the frequency of its occurrence is far too low to account for the observed intensity of the green line.[16] Also the suggested mechanism fails to account for the observed diurnal variations in the intensity of the [OI] lines.[16] For the same reason,

---

[16] According to Cabannes, *Comptes Rendus*, 1939, **208**, 1770, who favoured Chapman's theory, the green [OI] line and the Vegard-Kaplan bands are excited by the following processes:

$$3\,O\,(^3P) \rightarrow O_2\,(X\,^3\Sigma) + O\,(^1S) + 0{\cdot}92 \text{ volt} \qquad (a)$$

$$O\,(^3P) + O\,(^1D) + N_2\,(X\,^1\Sigma) \rightarrow N_2\,(A\,^3\Sigma) + O_2\,(X\,^3\Sigma) + O{\cdot}90 \text{ volt} \qquad (b)$$

While these processes are energetically possible, we shall show that they are far too infrequent to account for the observed intensities of the radiations and that they fail to account for the observed diurnal variations in the intensities of the radiations.

(1) The probability of the process (*a*) is certainly very small if the energy excess 0·92 volt must be transformed into the kinetic energies of the resulting particles. It may be somewhat greater if this energy excess is retained as energy of vibrational excitation of the $O_2\,(X\,^3\Sigma)$ molecule. Even then, the probability must be very much smaller than the gas kinetic value since the spin rule is not satisfied in this case. Assuming, for the optimum situation, that it is of the same order as the gas kinetic value, then the cross-section q for unit concentration of the third body is $\simeq 10^{-40}$ cm.[5] With this value of q, even a concentration of 10^{11}/c.c. for $O\,(^3P)$ would generate $O\,(^1S)$ by the process (*a*) only at the rate of about 1 per c.c. per second. This is too small to account for the observed intensity of the green line, which calls for some 10^2 $O\,(^1S)$ per c.c. Higher concentrations for $O\,(^3P)$ are not available above the E layer, and according to Cabannes and Dufay, the radiations of the night sky come from above the E layer.

(2) Similar considerations show that no three-body processes are adequate in providing for a high enough concentration of $O\,(^1D)$ to account for the intensities of the red [OI] lines.

(3) If the green [OI] line is excited by the process (*a*), then as the concentration of $O\,(^3P)$ decreases, the rate of production of $O\,(^1S)$ would also decrease. This would mean a continual decrease, however slow, in the intensity of the green line in the night. Also, if the $O\,(^1D)$ are supposed to be produced as the result of the emission of the green line, then on account of the longer lifetime of the $O\,(^1D)$, the concentration of $O\,(^1D)$ would first increase until the rate of production is balanced by the rate of disappearance by the emission of the red lines and by other quenching collisions. This would mean that the red lines increase in intensity immediately after sunset and reach a constant value shortly afterwards. But these are just opposite to the observed variations, namely: the green line increases in intensity after sunset to a maximum near midnight, and the red lines are most intense immediately after sunset and decline in intensity thereafter.

(4) If the $N_2\,(A\,^3\Sigma)$ responsible for the emission of the Vegard-Kaplan bands are excited by the process (*b*), then, assuming again for the sake of argument the optimum value $q \simeq 10^{-40}$ cm.[5] for the cross-section of the process for unit concentration of the third body $N_2\,(X\,^3\Sigma)$, one would need a concentration of 10^{10}/c.c. for $O\,(^1D)$, of 10^{11}/c.c. for $O\,(^3P)$ and 10^{12}/c.c. for $N_2\,(X\,^1\Sigma)$ in order to produce one $N_2\,(A\,^3\Sigma)$ molecule per c.c. per second. Such a rate of production of $N_2\,(A\,^3\Sigma)$ is much too low to account for the osberved total intensity of the Vegard-Kaplan bands, although the requisite concentration of $O\,(^1D)$ is already neither provided for by any process nor consistent with the observed intensity of the red lines.

The above estimates are made on the assumption that the cross-sections for the three-body processes have the gas kinetic values. When account is taken of the fact that the cross-sections are probably very much smaller than the gas kinetic values, the inadequacy of the mechanisms such as (*a*) and (*b*) becomes even more obvious.

the suggestion that the molecule of O_2 is dissociated into the atoms O (^{3}P) and O (^{1}S) by active nitrogen,[17] namely,

$$N_2\,(A\ ^3\Sigma) + N\,(^2P) + O_2\,(X\ ^3\Sigma) \rightarrow N_2\,(X\ ^1\Sigma) + N\,(^4S) + O\,(^3P) + O\,(^1S) + 0{\cdot}4 \text{ volt},$$

is unsatisfactory. Here we suggest the process Q_5 as the main process for the production of O (^{1}S). That the metastable O_2 ($C^3\Sigma$) should play the important intermediate rôle is not implausible if one remembers that the metastable N_2 ($A\ ^3\Sigma$) molecules are known to play a fundamental rôle in the upper atmosphere and the laboratory afterglow (as shown by the emission of the Vegard-Kaplan bands), and that the metastable O_2 ($C\ ^3\Sigma$) bears a similar relation to processes involving the oxygen atoms and molecules as N_2 ($A\ ^3\Sigma$) to those of nitrogen.

From the measured intensity of the green line in the night sky, Rayleigh has estimated that it corresponds to approximately 10^8 transitions per second in a column of the atmosphere of 1 sq. cm. base.[18] This, together with the transition probability $A_{green} \simeq 2$/sec,[19] requires that there be at least some 10^2 O (^{1}S) atoms produced per c.c. per second during the night. Assuming now that these are supplied by the process Q_5, we have

$$Q_5\,[O_2C\ ^3\Sigma]^2 \geqslant 10^2/\text{sec. c.c.}$$

Then, for a value of the cross-section of Q_5 lying between $10^{-3} - 10^3$ times the gas kinetic value, we have, respectively,

$$[O_2\,C\ ^3\Sigma] \geqslant 5 \times 10^7 - 5 \times 10^4/\text{c.c.}$$

for the necessary concentration of O_2 ($C^3\Sigma$) to maintain the excitation and emission of the green line. To show that such concentrations of O_2 ($C\ ^3\Sigma$) are not impossible, we have only to remember that there is a high concentration of O (^{3}P) for the production of O_2 ($C\ ^3\Sigma$) by the process Q_4. If there are some 10^{10} O (^{3}P) atoms per c.c. in the upper atmosphere just after sunset, and if the probability of radiative recombination Q_4 is of the order of 10^{-6} per collision, then the O_2 ($C\ ^3\Sigma$) are produced by Q_4 at a rate of $\sim 10^4$/sec. c.c. On assuming a high metastability of the O_2 ($C\ ^3\Sigma$), it will take some 10 minutes to build up a concentration of O_2 ($C^3\Sigma$) of the order 10^6/c.c. which is of the correct order of magnitude to account for the

[17] E. W. Hewson, *Rev. Mod. Phys.*, 1937, **9**, 420.

[18] Lord Rayleigh, *Proc. Roy. Soc.*, 1930, **A 129**, 458.

[19] E. U. Condon, *Astrophys. Jour.*, 1934, **79**, 217.

maintenance of the green line.* This building up of the concentration of $O_2(C\,^3\Sigma)$ by the process Q_4 may be responsible for the observed slight rise of the intensity of the green line towards midnight.[3, 4] The slight decline in the intensity of the line in the latter part of the night[4] may be due to the gradual depletion of the oxygen atoms through the various recombination processes, three-body as well as radiative.

Neglecting the recombination processes compared with the other collisions, we have for the rate of change of the concentration of $O(^1S)$

$$\frac{d[O\,^1S]}{dt} = Q_5[O_2C\,^3\Sigma]^2 + Q_{19}[N\,^2D][O\,^1D] - \{A_{green} + A_{trans} + (Q_9 + Q_9')[N_2A\,^3\Sigma] + Q_{15}[N_2^+X\,^2\Sigma] + Q_{21}[N_a\,^2S]\}[O\,^1S] \quad (10)$$

where A_{trans} is the probability of the trans-auroral transition $^1S \rightarrow {}^3P$ in OI and is 0·18/sec.[19] This trans-auroral line is not observed in the night sky or the aurora since it lies just beyond the limit of transparancy of the atmosphere. Now for the green line to appear, it is necessary that the rate of quenching by the various processes in (10) be not very large compared with the rate of emission of the line, *i.e.*,

$$A_{green} \ll (Q_9 + Q'_9)[N_2A^3\Sigma] + Q_{21}[Na\,^2S] + Q_{15}[N^+{}_2X\,^2\Sigma].$$

In the night sky where the negative bands of N_2^+ are either not present or extremely weak, the last term can be neglected. A knowledge of the cross-sections of Q_9' and Q_{21} will enable us to set an upper limit to the concentrations of $N_2(A\,^3\Sigma)$ and sodium atoms. Thus assuming the cross-section for Q_9' to lie between 10^{-2} and 10^2 times the gas kinetic value, one obtains for $(N_2A\,^3\Sigma)$ an upper limit of 10^{13} and 10^9/c.c. respectively. The actual concentration of $N_2(A\,^3\Sigma)$, especially in the layer where the dissociation of O_2 but not that of N_2 is maximum, is probably very much smaller than

---

* On taking into account the loss of $O_2(C\,^3\Sigma)$ through the emission of the Herzberg bands $O_2(C\,^3\Sigma) \rightarrow O_2(X\,^1\Sigma)$ and the processes Q_5, Q_5', Q_{12}, Q'_{12}, the rise of the concentration of $O_2(C^2\,^3\Sigma)$ will be given by the equation

$$\frac{d[O_2C\,^3\Sigma]}{dt} = k - \alpha[O_2C\,^3\Sigma] - \beta[O_2C\,^3\Sigma]^2$$

where k stands for the constant rate of production by the process Q_4, α represents the combined result of the processes $O_2(C\,^3\Sigma) \rightarrow O_2(X\,^1\Sigma)$, Q_{12}, and Q'_{12} and β the result of Q_5 and Q_5'. From this one obtains

$$2\beta[O_2C\,^3\Sigma] = -\alpha + B\,\frac{1 - Ae^{-Bt}}{1 + Ae^{-Bt}},$$

where $B = \sqrt{4k\beta + \alpha^2}$ and $A = (B - \alpha)/(B + \alpha)$. It is seen that the concentration of $O_2(C\,^3\Sigma)$ will tend to a constant value $(B - \alpha)/2\beta$ after a time t depending on the values of k, α and β.

10^9/c.c. (see discussion on $[O_2\,C\,^3\Sigma]$ above, which are formed by processes analogous to those for $N_2\,(A^3\Sigma)$).

(*B*) *Red (OI) lines*: $^1D_2 \rightarrow {}^3P_{1,2}$

As emphasized in the summary in the introduction, the red (OI) lines of the night sky differ from the green line in their diurnal intensity variations. The O (^{1}S) atoms in the night sky are probably produced by the process Q_5. The O (^{1}D) atoms are, in addition to the analogous but less probable process Q_5' and the result of the emission of the green line, now produced by the process Q_{18} which now assumes greater importance than Q_{19} for the excitation of ^{1}S, since the initial rate of production of O (^{1}D) by the process Q_{18} may now be very large on account of the large concentrations of O (^{3}P) and N (^{2}D). Assuming as before that immediately after sunset, there are some 10^{10} O (^{3}P) and some 10^6 N (^{2}D) atoms per c.c,[20] if the cross-section of Q_{18} is taken to be of the order 10^{-2} times the gas kinetic value, the process Q_{18} will then produce O (^{1}D) at the rate of some 10^4/sec. c.c. This is amply sufficient to account for the observed intensity of the red lines. With the depletion of the N (^{2}D) by this and other processes, this rate of production of O (^{1}D) would have decreased rapidly after sunset had it not been for the replenishment of O (^{1}D) by the process Q_5' and the result of the emission of the green line. The result is a more gradual decrease in [O ^{1}D] in the early part of the night, followed by a more or less steady value when the rate of depletion by the various processes in equation (11) becomes equal to the rate of replenishment. This may explain the observed fact that the red lines have the greatest intensity immediately after sunset.[4] The different behaviour of the intensity variations of the green and the red lines is thus due to the different mechanisms for the production of the O (^{1}S) and O (^{1}D).

The rate of change of (O ^{1}D) is, again on neglecting recombinations,

$$\frac{d\,[O\,^1D]}{dt} = 2Q_5'\,[O_2C\,^3\Sigma]^2 + Q_{18}\,[O\,^3P]\,[N\,^2D] + A_{green}\,[O^1S] - \{A_{red} + Q_8\,[N_2A\,^3\Sigma] + Q_{16}\,[O_2X\,^3\Sigma] + Q_{19}\,[N\,^2D] + Q_{22}\,[Na\,^2S]\}\,[O\,^1D] \qquad (11)$$

where the transition probabilities A_{red} are $2{\cdot}5 \times 10^{-3}$ and $7{\cdot}5 \times 10^{-3}$ per second for the lines $^1D_2 \rightarrow {}^3P_1$ and $^2D_2 \rightarrow {}^3P_2$ respectively.[19] The red lines

[20] The value 10/c.c. for [N ^{2}D] is based on the following estimates: Kaplan pointed out the possible appearance of the lines $^2D \rightarrow {}^4S$ in NI with about 1/50 the intensity of the green [OI] line in Babcock's spectrum of the night sky (see C below). Since the lifetime of N (^{2}D) is of the order 10^5 second, this requires that there be at least some 10^6 N (^{2}D) per c.c. to account for the observed intensity.

are here quenched by the processes Q_8 and Q_{16}. As Q_8 and Q_{16} are probably of the same order of magnitude and as the concentration of the oxygen molecule in the normal state is certainly larger than that of the $N_2(A\,^3\Sigma)$ by some powers of 10, we need only consider the quenching by Q_{16}. The condition for the red lined to appear is hence

$$A_{red} \ll Q_{16}\,[O_2 X\,^3\Sigma].$$

Assuming that the cross-section for Q_{16} is 10^{-2} to 10^2 times the gas kinetic value, one finds that for the red lines to appear, $(O_2 X\,^3\Sigma)$ must not be very much greater than 10^{10} and 10^6/c.c. respectively. Even the value 10^{10}/c.c. is too low for the E layer where the concentration of O_2 is probably of the order $10^{11} - 10^{12}$/c.c. The above condition is more readily satisfied in the higher altitudes. This may be connected with the observed enhancement of the red lines in the sunlit auroræ[6] which are situated in very much higher altitudes (300 – 800 km.) than the ordinary auroræ (100 km), although the enhancement may also be due to the production of $O(^1D)$ by the photo-dissociation process (3).

Finally we may remark in passing that the great difference in the relative intensity of the green and the red lines in the night sky and in the nebulæ is not a matter of the difference in the gas pressures in the two cases alone. From equations (10) and (11), it is seen that were it not for the quenching collisions, the red lines would have been more intense than the green since any excitation of $O(^1S)$ by Q_5 would contribute to the intensity of the red lines on emission of the green line. That the red lines are weaker than the green is probably due to the more effective quenching of the former by Q_{16} (exciting at the same time the A, B, α bands of oxygen) than that of the latter by the process $O_2(X\,^3\Sigma) + O(^1S) \rightarrow O_2(A\,^1\Sigma) + O(^1D)$, since here the spin rule is violated. On the other hand, the extremely low pressure in the nebulæ renders quenching collisions of any kind unimportant, and the intensities of the green and the red lines are determined essentially by the relative frequencies of excitations of ^1S and ^1D. That the red lines are far more intense than the green line in the nebulæ is to be explained by the predominance of electrons having energies enough to excite ^1D but not ^1S. In fact, from the relative intensities of the red and the green lines and the theoretical excitation cross-sections of these states by electron impact, it has been possible to obtain very reasonable values for the temperatures of the nebulæ.[21]

---

[21] D. H. Menzel, L. H. Aller and M. H. Hebb, *Astrophys. Jour.*, 1941, **93**, 230.

(*C*) *Forbidden lines of* [*NI*] $^2D \rightarrow {}^4S$

The situation with the forbidden lines of NI can be expected to be similar to that with OI. The lines $^2P \rightarrow {}^2D$ have transition probabilities of the order 1/sec.; they lie in the infra-red $1{\cdot}04\,\mu$ and hence have not been observed. The lines $^2D \rightarrow {}^4S$ have the small transition probabilities of the order 10^{-5}/sec. Kaplan has recently succeeded in observing both the $^2D \rightarrow {}^4S$ and the $^2P \rightarrow {}^4S$ lines in afterglows in nitrogen under moderately high pressure, and has pointed out the probable appearance of $^2D \rightarrow {}^4S$ in Babcock's spectrogram of the night sky with an intensity about 1/50 that of the green [OI] line.[22] If this identification is correct, we may consider the equations

$$\frac{d\,[\mathrm{N}\ {}^2\mathrm{P}]}{dt} = Q_6''\,[\mathrm{N_2A}\ {}^3\Sigma]^2 - \{\mathrm{A}\,({}^2\mathrm{P} \rightarrow {}^2\mathrm{D}) + \mathrm{A}\,({}^2\mathrm{P} \rightarrow {}^4\mathrm{S}) + (Q_9 + Q_9')\,[\mathrm{N_2A}\ {}^3\Sigma] + Q_{14}\,[\mathrm{N_2^+X}\ {}^2\Sigma]\}\,[\mathrm{N}\ {}^2\mathrm{P}], \quad (12)$$

$$\frac{d\,[\mathrm{N}\ {}^2\mathrm{D}]}{dt} = 2\,Q_6'\,[\mathrm{N_2A}\ {}^3\Sigma]^2 + \mathrm{A}\,({}^2\mathrm{P} \rightarrow {}^2\mathrm{D})\,[\mathrm{N}\ {}^2\mathrm{P}] - \{\mathrm{A}\,({}^2\mathrm{D} \rightarrow {}^4\mathrm{S}) + (Q_{10} + Q_{10}')\,[\mathrm{N_2A}\ {}^3\Sigma] + Q_{17}\,[\mathrm{O_2X}\ {}^3\Sigma] + Q_{18}\,[\mathrm{O}\ {}^3\mathrm{P}] + Q_{19}\,[\mathrm{O}\ {}^1\mathrm{D}] + Q_{20}\,[\mathrm{Na}\ {}^2\mathrm{S}]\}\,[\mathrm{N}\ {}^2\mathrm{D}], \quad (13)$$

in which recombination processes have again been omitted. The initial concentrations of N (^{2}P) and N (^{2}D) immediately after sunset may be very large, especially at the level where the dissociation of N_2 is most intense. The large value of A (^{2}P$\rightarrow{}^2$D), however, reduced (N ^{2}P) rapidly to a low value so that the more or less steady but small concentration during the night is determined by the rate of the process Q_6'', which may be much smaller than the corresponding process Q_5 in the case of the excitation of O (^{1}S) on account of the very much larger energy discrepancy (1·3 volt *vs.* 0·12 volt). On the other hand, the small value A (^{2}D$\rightarrow{}^4$S) can be consistent with a considerably higher value of [N ^{2}D]. This may be the reason why the nebular $^2D \rightarrow {}^4S$ can be observed while the trans-auroral $^2P \rightarrow {}^4S$ at 3466 A with a much greater transition probability cannot.[23]

(*D*) *Negative bands of* N_2^+ N_2^+: $(B\ {}^3\Sigma) \rightarrow N_2^+\,(X\ {}^2\Sigma)$

Once we have assumed the generation of N_2^+ by solar radiations by such process as (7), it is not necessary to assume other modes of generation during the night when one remembers the low rate of loss of N_2^+ by recombination processes. In fact, that the N_2^+ bands are greatly enhanced

[22] J. Kaplan, *Phys. Rev.*, 1939, **56**, 858; 1940, **57**, 249.

[23] R. Bernard, *Phys. Rev.*, 1939, **55**, 511; Elvey, Swings and Linke, *Astrophys. Jour.*, 1941 **93**, 337.

relative to the green [OI] line in sunlit auroræ[24] and that the N_2^+ bands in the night sky increase in intensity when the last trace of sun light touches the uppermost part of the atmosphere in the evening and when the first trace of sun light reaches the top of the atmosphere at the dawn[25] are consistent with the view that the N_2^+ are produced by solar radiations. It is true that the very much greater intensity of the N_2^+ bands in the auroræ than in the night sky cannot be explained without additional hypotheses about the auroræ. But granting a higher concentration of N_2^+ in the aurora, one can then understand why the N_2^+ bands are strong and the Vegard-Kaplan bands are weak in the aurora and conversely in the night sky; for the N_2^+ bands excited by the process Q_{13} are at the expense of the metastable $N_2(A\ ^3\Sigma)$, thus quenching the Vegard-Kaplan bands (see below on Vegard-Kaplan bands).

As summarized in the introduction, the strongest N_2^+ bands in the aurora and the night sky are the $v'-v''=0-0;\ 0-1;\ 0-2;\ 1-2;\ 1-3;\ 2-3$ bands. The strong enhancement of transitions from $v'=0, 1, 2$ may be ascribed to the excitation processes Q_{14} and Q_{15}. The enhancement of the N_2^+ bands in sunlit aurora and sunlit atmosphere is also consistent with this view since the concentrations of N (^{2}P) and O (^{1}S) generated by sun light by the processes (1), (2), (3) and possibly also (6) and (8) will be high in the sunlit regions. The tarnsition $v'=11\rightarrow v''=13$ has a wave-length 4233·5 A for the band centre so that its head falls just on top of the 4236 (1→2) bands. Also the $v'=12\rightarrow v''=13$ band has the wave-length 3915 and may contribute partly to the great intensity of the 3914 (0→0) band. This may perhaps account for the excitation of the N_2^+ bands by $N_2(A\ ^3\Sigma)$.

(*E*) *Second positive bands*: $N_2(C\ ^3\Pi)\rightarrow N_2(B\ ^3\Pi)$

The only plausible processes for the excitation of the second positive system of N_2 are Q_6 and Q_{12}. The equation for $[N_2(C\ ^3\Pi)]$ is

$$\frac{d\,[N_2C\ ^3\Pi]}{dt} = Q_6\,[N_2A\ ^3\Sigma]^2 + Q_{12}\,[N_2A\ ^3\Sigma]\,[O_2C\ ^3\Sigma] - A_{2nd}\,[N_2C\ ^3\Pi] = 0. \qquad (14)$$

Here no quenching collisions need be considered. The process Q_{12} will be able to excite $v'=0$ of C $^3\Pi$ only when the $N_2(A\ ^3\Sigma)$ is initially in a state $v=1$ (see end of G) below, while the 10550 cm.$^{-1}$ energy available in the process Q_6 can either all go into the excitation of $N_2(B\ ^3\Pi)$, or be divided

[24] C. Störmer, *Zeits. f. Geophys.*, 1929, **5**, 185.
[25] V. M. Slipher, *Monthly Notices, R.A.S.*, 1933, **93**, 657.

between the vibrational motions of the two resulting molecules. In the first case, the bands from $v' = 0$ will be enhanced; in the second case, all bands up to $v' = 5$ can be excited, with perhaps some enhancement of $v' = 1, 2$. As seen from the summary in the introduction, these are in general agreement with the observed facts.

(*F*) *First positive bands*: $N_2(B\,^3\Pi) \rightarrow N_2(A\,^3\Sigma)$

The first positive bands are the characteristic feature of the night sky, the aurora and the afterglow in nitrogen. In the afterglow, Kaplan has succeeded in exciting the $v' - v'' = 3$ sequence with intensity maxima corresponding to $v' = 10$ and $v' = 6$. These enhancements have been explained as due to the processes Q_9 and Q_{10}. In the aurora, Vegard observed the bands $v' = 10 \rightarrow v'' = 7$ at 6323 A. and $v' = 7 \rightarrow v'' = 6$ at 7880 A. These seem to indicate the processes Q_9 and Q_{10}. In the night sky, bands from very high vibrational levels such as $v' = 15$, 16 have been found. These excitations are furnished by the processes Q_7, Q_8 and Q_{12}'. These together with Q_9 and Q_{10} may account for the excitation of bands from $v' = 4$ to $v' = 15$ or higher observed in the night sky by Cabannes and Elvey, Swings and Linke.[3, 4]

(*G*) *Vegard-Kaplan bands*[26] N_2: $(A\,^3\Sigma) \rightarrow N_2(X\,^1\Sigma)$

The equation for the rate of change of $[N_2A^3\Sigma]$ is

$$\frac{d\,[N_2A\,^3\Sigma]}{dt} = Q_1\,[N\,^4S]^2\,[X] + Q_3\,[N\,^4S]^2 -$$

$$\{A_{V.K} + (Q_6 + 2\,Q_6' + 2\,Q_6'')\,[N_2A\,^3\Sigma] + Q_7'\,[O\,^1S] + Q_9'\,[N^2\,P] + Q_{10}\,[N\,^2D] + Q_{11}\,[O_2X\,^3\Sigma] + Q_{13}\,[N_2{}^+X\,^2\Sigma]\}\,[N_2A\,^3\Sigma]$$

As the Vegard-Kaplan bands arise from transitions violating the selection rule for the multiplicity, they have small transition probabilities. Accordingly they will be emitted only if

$$A_{V.K} \ll \{Q_6 + 2\,Q_6' + 2\,Q_6''\}\,[N_2A\,^3\Sigma] + Q_7'\,[O\,^1S] + Q_9'\,[N\,^2P] + Q_{10}'\,[N\,^2D] + Q_{11}\,[O_2X\,^3\Sigma] + Q_{13}\,[N_2{}^+X\,^2\Sigma]. \qquad (15)$$

Thus the emission of these bands requires a low $[N_2{}^+X\,^2\Sigma]$ and of course the absence of ultraviolet radiations that may destroy the N_2 $(A\,^3\Sigma)$ by

[26] This "complementary" nature of the negative bands of $N_2{}^+$ and the Vegard-Kaplan bands is true not only of the aurora and the night sky, but seems to be true also in the discharge tube. In the afterglow produced by a feeble discharge, Kaplan (*Pub. Astron. Soc. Pacif.*, 1935, **47**, 257), found that the Vegard-Kaplan bands are enhanced relative to the second positive bands while the $N_2{}^+$ bands are absent. On the other hand, when the $N_2{}^+$ bands are strong, the Vegard-Kaplan bands are not found (Kaplan, *Phys. Rev.*, 1932, **42**, 807).

the processes (6) and (7). This is in agreement with the fact that in the sunlit aurora where the N_2^+ bands are strong and hence $[N_2^+ X\ ^2\Sigma]$ high, the Vegard-Kaplan bands are weak, while in the night sky where the N_2^+ bands are weak, the Vegard-Kaplan bands are strong.

It is observed that the blue radiations of the night sky reach a maximum intensity immediately after midnight,[27] like the green [OI] line. Now the strongest radiations in the blue region are the 4171 and 4425 bands of the Vegard-Kaplan system. A rise of intensity of these bands in the first part of the night may be due to the same cause as that for the green line, namely, the building up of the concentration of the metastable $N_2(A\ ^3\Sigma)$ by the processes Q_1 and Q_3. Its decline in the second part of the night can be ascribed to the gradual depletion of the N atoms.

In the night sky, Vegard-Kaplan bands from all levels v' up to 7 are observed, the bands from $v' = 2, 3, 4$ being particularly enhanced. It is of course not possible to say anything about the populations of the different levels of the $N_2(A\ ^3\Sigma)$ resulting from the radiative process Q_3. But those produced by the process Q_1 may be in any state v' up to 7 since the energy available in the process is 1·2 volt. There may be a preponderance of levels $v' = 2, 3, 4$ corresponding to the division of this energy between the two resulting molecules $N_2(A\ ^3\Sigma)$ and $N_2(X\ ^1\Sigma)$. Also the large number of $N_2(A\ ^3\Sigma)$ molecules resulting from the emission of the first positive bands $v' = 6, 7 \rightarrow v'' = 3, 4$ would enhance the Vegard-Kaplan bands from $v' = 3, 4$.

In discussing the enhancement of certain bands in a system involving allowed transitions, it is necessary only to consider the levels excited with close resonance since the lifetimes of these states are so short that a redistribution by collisions can be neglected. With the Vegard-Kaplan bands, on account of the long lifetime of the metastable state $A\ ^3\Sigma$, it is necessary to consider the effect of collisions between the $N_2(A\ ^3\Sigma)$ molecules and other particles. It is known, however, both experimentally and theoretically that the probability of energy transfer between the vibrational motion of a molecule and the translational motion of an atom or a molecule is very small, of the order $10^{-7} - 10^{-6}$ per collision.[28] As the collision frequency of an atom or a molecule with other molecules is of the order 10^3 per second at the pressure of the E layer, it is clear that de-excitation of vibrational excitation by collisions is unimportant. This persistence of vibrational excitation accounts for the emission of Vegard-Kaplan bands from rather high levels v.

---

[27] N. E. Bradbury and W. T. Sumerlin, *Phys. Rev.*, 1940, **57**, 249.

[28] *Cf.* Mott and Massey, *Theory of Atomic Collisions*, Oxford Univ. Press, 1933, p. 249.

(*H*) *Lyman-Birge-Hopfield Bands*: $N_2(a\,^1\Pi) \rightarrow N_2(X\,^1\Sigma)$

The existence of these bands, especially those from $v' = 0$ to $v'' = 19-23$, has recently been made plausible by the observations and identifications of Elvey, Swings and Linke.[4] It is suggested here that this system of bands is excited from the metastable $N_2(A\,^3\Sigma)$ by the metastable $N(^2D)$, $N(^2P)$ and $O(^1S)$ by the processes Q_{10}', Q_9', Q_7' respectively. While $N(^2P)$ and $O(^1S)$ can excite the vibrational levels $v' = 6$ and 9 respectively, $N(^2D)$ excites $v' = 0$ with almost exact resonance (energy discrepancy $\simeq 1/400$ of a volt). This may account for the enhancement of the bands 3378 ($0 \rightarrow 19$), 3834 ($0 \rightarrow 21$), 4420 ($0 \rightarrow 23$). The possible appearance of bands from $v' = 10$ or higher may arise from excitations by $O(^1S)$ of $N_2(A\,^3\Sigma)$ initially in the vibrational levels $v = 1$, 2 or 3. That this is possible is seen from the foregoing discussion of the persistence of vibrational excitation.

The equation for the rate of change of $[N_2 a\,^1\Pi]$ is

$$\frac{d[N_2 a\,^1\Pi]}{dt} = \{Q_7'[O\,^1S] + Q_9'[N\,^2P] + Q_{10}'[N\,^2D]\}[N_2 A\,^3\Sigma] - A_{LBH}[N_2 a\,^1\Pi] = 0. \qquad (16)$$

Again no quenching collisions need be considered here.

(*I*) *Atmospheric bands of* O_2 O_2: $(A\,^1\Sigma) \rightarrow O_1(X\,^3\Sigma)$

If the existence of the "A", "B", "a", "a'", "a''" bands of O_2 corresponding to the transitions $0 \rightarrow 0$, $1 \rightarrow 0$, $2 \rightarrow 0$, $3 \rightarrow 0$, $4 \rightarrow 0$ respectively in the night sky is established, then a mechanism for the excitation of the first three is provided by the process Q_{16} and one for the last two by Q_{17}. These processes are responsible for the partial quenching of the "nebular" lines in [OI] and [NI] respectively.

(*J*) *Schumann-Runge bands of* O_2 O_2: $[B\,^3\Sigma] \rightarrow O_2(X\,^3\Sigma)$

The observations of Dufay, Gauzit, Elvey, Swings and Linke suggest very strongly the presence of the Schumann-Runge bands in the night sky, especially those from the levels $v' = 0$ and 1. A mechanism for the excitation of these bands is provided by the process Q_{11} whose cross-section may not be small since the energy discrepancy for excitation of $v' = 0$ is only 1/20 of a volt.

(*K*) *Na lines*: $^2S - ^2P$

The yellow lines of sodium have been observed in the night sky and various aspects of the problem concerning it have been discussed by a number of authors. Chapman suggested the process Q_{22} for the excitation mechanism and accounted for the energy deficiency of 0·14 volt by means

of the kinetic energy of the particles.[29] The fraction, however, of atoms having this kinetic energy is very small unless the temperature of the atmosphere has a value above 1000° K., for which there does not seem to be very strong evidence (see foot-note 30 below). On the other hand, the process Q_{20} is energetically more probable, and on account of the smaller transition probabilities A ($^2D \rightarrow {}^4S$) than those for the red [OI] lines, the concentration of N (^2D) may be greater than that of O (^1D). The process Q_{21} has an even higher cross-section since the resonance is closer and the spin rule is satisfied. This may make up for the low concentration of O (^1S) and has to be taken into account in assessing the relative importance of the various processes for the excitation of the Na lines. More information concerning the variations of the intensity of the Na lines with time and altitude is necessary for a proper understanding of the problem of atmospheric sodium.

(*L*) *Water vapour bands*

According to Cabannes, the water vapour bands at $0{\cdot}59\,\mu$, $0{\cdot}65\,\mu$, $0{\cdot}698\,\mu$, $0{\cdot}72\,\mu$ corresponding to $4\,\nu_1+\nu_3$, $3\,\nu_1+\nu_2+\nu_3$, $\nu_1+3\,\nu_3$, $3\nu_1+\nu_3$ respectively are present in the spectrum of the night sky, and possibly also in the aurora.[3] These bands, if their existence is established, are interesting in that they differ from all the other radiations in being pure vibration-rotational bands. The most effective modes of excitation would be a collision of the first kind with another atom or molecule, or a collision of the second kind with a molecule in a vibrationally excited state. The probability of the first collision is extremely small, and the fraction of particles having a kinetic energy of the order of 1 volt must be exceedingly small. On the other hand, molecules in highly vibrationally excited states [such as $v=13$, 14, 15 in $N_2(X\,{}^1\Sigma)$ as the result of the Vegard-Kaplan transitions] may be fairly abundant, and it is possible that these molecules are responsible for the excitation of the water vapour bands by a resonance process.

The existence of these high combination, and hence weak, water vapour bands in the night sky would indicate appreciable concentration of water vapour in the upper atmosphere. As water vapour plays the most important part in the problem of radiative equilibrium of the earth's atmosphere, it would be desirable to have some measurements of the absolute intensities

[29] S. Chapman, *Astrophys. Jour.*, 1939, **90**, 309. The mechanism $NaO + O \rightarrow Na + O_2$ suggested there for the maintenance of free Na atoms in the presence of oxygen has to be considered not only from the point of view of energies, but also together with the fact that the process involves an activation energy approximately equal to the dissociation energy of NaO. At the temperature of the upper atmosphere, such a process will be exceedingly improbable.

and some theoretical estimates of the transition probabilities of these bands so that one may estimate the concentration of water vapour, and hence the temperature, of the upper atmosphere.[30]

(*M*) *Other radiations*

It seems to be generally agreed that in the spectra of the night sky and the aurora, there are no atomic lines other than the lines of [OI] and possibly the $^2D \rightarrow {}^4S$ of [NI].[31] The absence of the atomic lines of N, O as well as H and other rare gases is now understandable since the energies available for excitation in the metastable atoms and molecules of nitrogen and oxygen do not exceed 6·1 volts. In fact, the strong point of the proposed mechanisms here is that they provide a reasonable process for each of the radiations observed and at the same time allow satisfactorily for the absence of others that are not observed.

Concerning the possible presence of bands from such molecules as NO, NH, CH and CN, the observational material is still too meagre to warrant any discussion. In any case, the bands, if they are definitely confirmed, are so weak and so scanty that these molecules must be very rare in the upper atmosphere. The absence or scarcity of NO alone perhaps

---

[30] It seems that no accurate knowledge concerning the temperature of the upper atmosphere of the earth is available. Vegard (quoted in Rosseland's *Theoretical Astrophysics*, Oxford Univ. Press, 1936, pp. 234–37) has estimated the temperature of the aurora from the intensity distribution in the unresolved 4278 A. band of N_2^+ and found a value 70° C. This can only be a rough estimate on account of the low dispersion of the spectrum. [The formula on p. 234 for the intensity of a rotational line in a band, namely, $I(j \rightarrow j+1) \propto (2j+1) \exp.(-E_j/kT)$, is slightly in error as it does not take into account the factor depending on the transition probability of the line. The correct expression is $(j+1) \exp.(-E_j/kT)$]. More recently, from the R branch of the 4278 band, Vegard and Tonsberg, *Geofys. Pub.*, 1938, **12**, 3, obtain a temperature of − 35° C. In any case, the temperature so determined will represent the temperature of the atmosphere only if the excitation process does not greatly change the distribution in the rotational states, for example, if the bands are excited by electron impact. On the other hand, if the bands are excited by collisions of the second kind with heavy particles, the temperature parameter determined from the intensity distribution in a band may differ from the thermal temperature in a way depending on the probability of energy transfer to and from the rotational motion in such collisions.

On the basis of the theory of intensities of electronic transitions and the intensity distribution in the negative bands of N_2^+ and the positive bands of N_2, Rosseland and Steensholt (quoted in Rosseland's book, p. 244) have also calculated the temperature of the aurora and found values of the order 2000°−3000° K. As emphasized by Rosseland, these values must not be taken to mean the temperature of the atmosphere since the bands are assumed to have been excited by swift particles not in thermal equilibrium with the atmosphere. On our view here, the bands are excited by collisions of the second kind. The intensity distribution in a band system depends then only on the resonance mechanism and has nothing to do with the temperature of the atmosphere at all.

[31] For the aurora spectrum, M. Nicolet, *Ann. d'Astrophys.*, 1938, **1**, 381 ; for the night sky, Elvey, Swings and Linke, *Astrophys. J.*, 1941, **93**, 337.

needs some consideration, in view of the abundance of the N and O atoms. This is probably because of the fact that the layers of maximum dissociation of the nitrogen and the oxygen molecules, and hence the layers of maximum concentration of the N and O atoms, are different. Thus while a concentration of O atoms of 10^{10}/c.c. will lead to a recombination into O_2 at a rate of 10^4/sec. c.c., the presence of N atoms at the same layer with a concentration 10^6/c.c. will lead to the formation of only 1 NO per sec. per c.c.

Concluding Remarks

To sum up, then, it is seen from the present theory that the various emission processes take place at the expense of the energies of excitation of the metastable atoms and molecules of N and O, and these metastable atoms and molecules are constantly replenished by the recombinations of the atoms generated by photo-dissociation during the day. It is interesting to note that the various processes do not all proceed in one direction alone, with a consequent rapid depletion of the metastable atoms or molecules. Rather many of these processes form cycles so that continual excitation and emission of the various radiations are possible. The overall result of all the processes is, of course, the recombinations of the atoms into molecules. For example, from equations (12), (13), (15), (16) and the following ones

$$\frac{d[N\,{}^4S]}{dt} = \{Q_6'' [N_2A\,{}^3\Sigma] + (Q_9 + Q_9')[N\,{}^2P] + (Q_{10} + Q_{10}')[N\,{}^2D]\}[N_2A\,{}^3\Sigma] + \{Q_{17}[O_2X\,{}^3\Sigma] + Q_{18}[O\,{}^3P] + Q_{19}(O\,{}^1D) + A({}^2D \rightarrow {}^4S)\}[N\,{}^2D] + Q_{14}[N_2{}^+X\,{}^2\Sigma][N\,{}^2P] - 2(Q_1[X] + Q_3)[N\,{}^4S]^2, \quad (17)$$

$$\frac{d[N_2X\,{}^1\Sigma]}{dt} = \{(Q_6 + Q_6' + Q_6'')[N_2A\,{}^3\Sigma] + Q_{13}[N_2{}^+X\,{}^2\Sigma] + A_{V.K}\}[N_2A\,{}^3\Sigma], + A_{LBH}[N_2{}^\alpha\,{}^1\Pi], \quad (18)$$

we have, as we expect,

$$\frac{d}{dt}\{[N\,{}^4S] + [N\,{}^2D] + [N\,{}^2P] + 2[N_2X\,{}^1\Sigma] + 2[N_2A\,{}^3\Sigma]\} = 0. \quad (19)$$

As $\frac{d}{dt}[N_2X\,{}^3\Sigma]$ must be positive since in the absence of sunlight no collision process can lift the N_2 molecule from the normal state or dissociate it, and as $\frac{d}{dt}[N_2A\,{}^3\Sigma]$ must be $\simeq 0$ in the steady (or very slowly varying) state during the night when the intensity of the Vegard-Kaplan bands does not vary greatly, it follows that

$$\frac{d}{dt}\{[N\,{}^4S] + [N\,{}^2D] + [N\,{}^2P]\} < 0,$$

i.e., the net result of the various processes is a steady decrease in the concentrations of the atoms. Entirely similar result holds for the processes

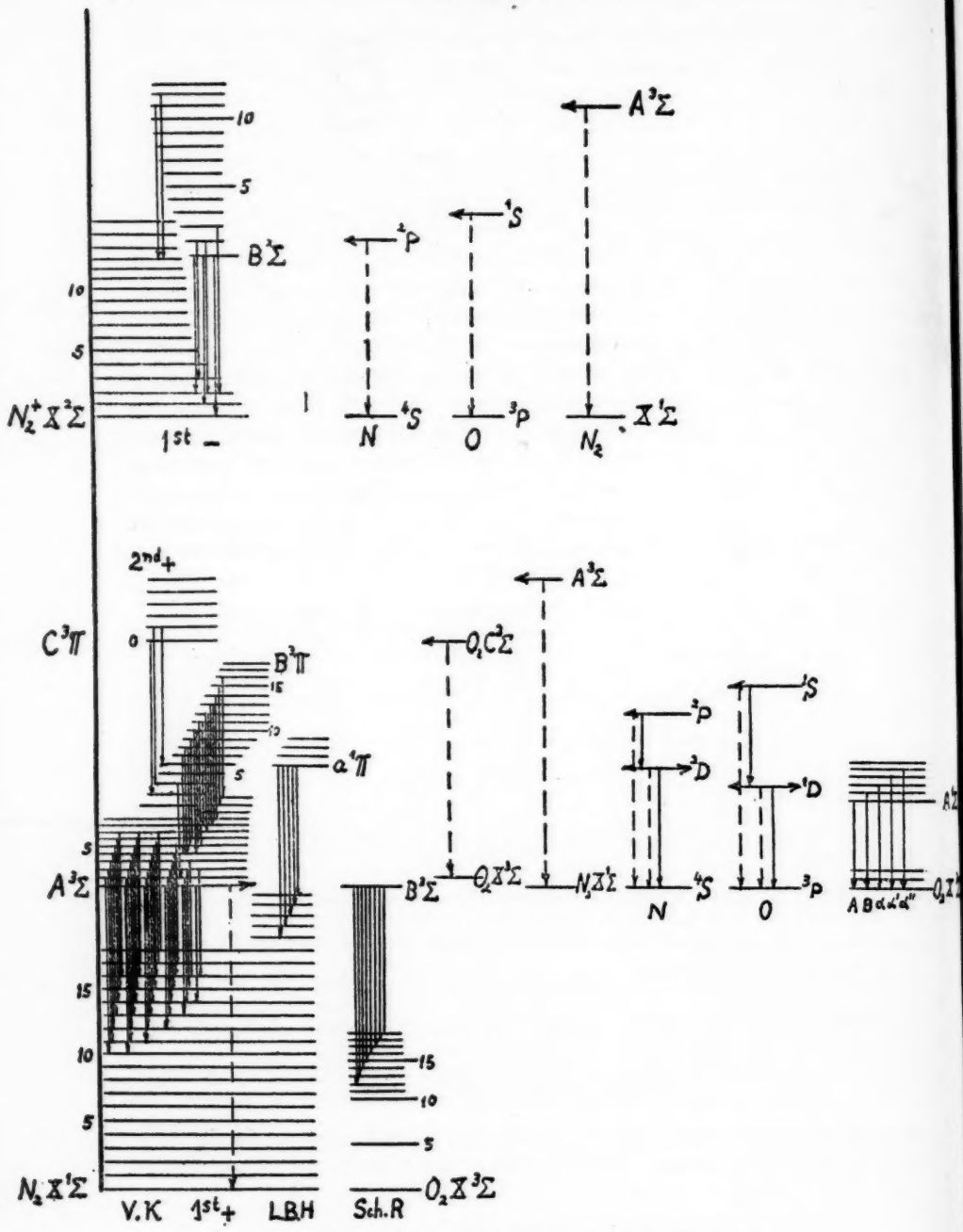


FIG. 1. Energy levels involved in the collisional excitations and radiative transitions in the night sky and the aurora

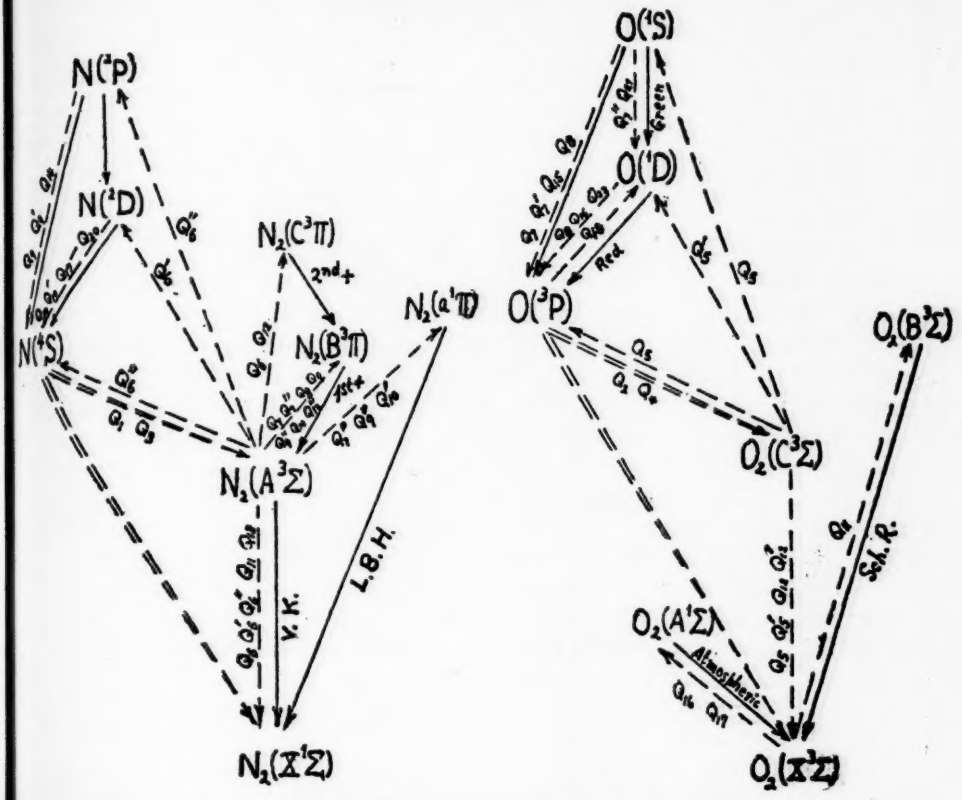


FIG. 2. Excitation processes in the night sky and the aurora
Solid lines indicate radiative transitions ; dashed lines represent excitation collisions

involving the oxygen atoms and molecules. The O atoms disappear either through the radiative processes of the type Q_4 or through three-body processes of the type Q_2, followed by processes Q_5, Q_{12} and others, ending eventually in the normal state $O_2(X\,^3\Sigma)$. The various processes and their interrelations are rendered clear by the diagrams in Figs. 1 and 2.

Finally we need only add that the rates of the various processes of excitation and radiation depend either directly or indirectly on the rates of supply of the metastable $N_2(A\,^3\Sigma)$ and $O_2(C\,^3\Sigma)$ molecules, which in turn depend on the rates of recombination of the atoms. As these recombinations are the bottle-neck of the various processes, we need only consider them in order to see if the supply of atoms at sunset will last through the

night. That they will last is seen from our estimate of the rate of recombination of the O atoms in connection with the discussion of the green [OI] line.

Summary

It is shown that the main features in the selective emission spectra of the night sky and the aurora, namely, the forbidden [OI] lines, the various systems of bands of N_2^+ and N_2 and O_2, and in particular, the enhancement of certain lines and bands relative to others and the diurnal variations of the intensity of certain lines in the night sky, can be satisfactorily explained on the view that all the excitation and quenching processes in the upper atmosphere are collisions of the second kind, of the resonance type, between the metastable atoms and molecules of nitrogen and oxygen. The metastable atoms are generated in the night by collisions between the metastable molecules; the latter are in turn formed by the recombinations of the normal atoms which are produced by photo-dissociation of the molecules during the day. A strong argument for the theory is that, not only the observed radiations are provided with reasonable excitation processes, but the absence of other atomic lines N, O, H and the rare gases is automatically accounted for by the maximum energy available for the excitations in these metastables, which is only 6·1 volts (the energy of N_2 [A $^3\Sigma$]). It is suggested that these processes in Table II are the microscopic processes responsible for the observed spectra, while such large-scale features as the shapes of the auroræ and seasonal variations in the intensities, etc., may have to be explained by further hypotheses.

OPTICAL THEORY OF CHROMATIC EMULSIONS AND OF THE CHRISTIANSEN EXPERIMENT

By G. N. Ramachandran

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received July 2, 1943

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

While engaged upon some determinations of the refractive index of transparent powders by the method of immersing them in liquid mixtures of the same refractive index, Christiansen (1884) observed some very remarkable and interesting colour effects. If white light was employed, the transmitted light was highly coloured, the colour corresponding to the particular wave-length for which the two substances have the same refractive index. Lord Rayleigh (1885) repeated these experiments, and found that the transmitted spectrum was remarkably narrow. The subject was investigated in detail by Sethi (1921), who studied the effect of the size and number of the particles and of the thickness of the medium on the transmitted light, and also the light scattered in other directions. He extended his studies to the colours shown by emulsions of immiscible liquids, whose refractive indices are equal for some wave-length in the visible range. The elegant method of preparing these emulsions in a stable state, discovered by Holmes and Cameron (1922), enabled Sogani (1926) to make a thorough study of the phenomena exhibited by these "chromatic emulsions".

Lord Rayleigh has rightly remarked (1899) that a proper theory of the Christiansen phenomenon must be based on wave-optical ideas. Following the lines suggested by Rayleigh, both Sethi and Sogani have tried to explain, theoretically, the phenomena observed by them. But their method is not comprehensive, since separate theories have to be worked out to explain the transmission colours, and the colours of the light scattered in other directions. In this paper, an attempt is made to explain the whole range of phenomena on a single theory based on the diffraction of light by a transparent sphere, whose refractive index is not appreciably different from that of the surrounding medium. The author (1943 *a*) has already developed such a theory in connection with the study of the transmission of light through a cloud of transparent droplets. As a particular case, the theory

has been used to explain the occurrence of coronæ when a bright object is viewed through thin cloud (1943 *b*).* The application of the theory to the explanation of the properties of chromatic emulsions forms another particular case, not covered by the previous one. The theory is strictly applicable only to spherical particles, and hence only to the case of chromatic emulsions; nevertheless as we shall see in the course of the paper, it suffices to give a good account of the phenomena observed in the Christiansen experiment with particles of arbitrary shape.

2. Intensity and Spectral Nature of the Transmitted Light

If a sphere of radius a, and of refractive index μ, be placed in a medium of refractive index μ_0, then the amplitude of the wave diffracted in a direction making an angle ϕ with the incident direction can be shown (1943 *a*) to be

$$X = X_1 - X_2, \tag{1}$$

where
$$X_1 = K \sin \chi \int_0^{\pi/2} J_0(\eta \sin \theta) \cos(\xi \cos \theta) \sin \theta \cos \theta \, d\theta$$
$$- K \cos \chi \int_0^{\pi/2} J_0(\eta \sin \theta) \sin(\xi \cos \theta) \sin \theta \cos \theta \, d\theta, \tag{2}$$

$$X_2 = K \sin \chi \cdot J_1(\eta)/\eta, \tag{3}$$

$$\xi = 4\pi(\mu - \mu_0) a/\lambda, \ \eta = 2\pi a \mu_0 \sin(\phi)/\lambda \text{ and } K = 2\pi a^2/\lambda, \tag{4}$$

the incident wave being represented by $\sin \chi$, and λ being its wave-length in vacuum.

In the exact forward direction, however, the effect of the incident wave would also be present. If we denote the amplitude due to the incident wave as X_0, then that due to the transmitted wave is

$$X' = X_0 + X_1' - X_2' \tag{5}$$

where X_1' and X_2' are the values of X_1 and X_2 when $\phi = 0$. For this case, $\eta = 0$, and the integrals in (2) can be integrated (1943 *a*) giving

$$X' = X_0 + K \sin \chi \left\{ \frac{\cos \xi}{\xi^2} + \frac{\sin \xi}{\xi} - \frac{1}{\xi^2} - \frac{1}{2} \right\}$$
$$- K \cos \chi \left\{ \frac{\sin \xi}{\xi^2} - \frac{\cos \xi}{\xi} \right\}$$
$$= X_0 - KC_1' \sin \chi - KS' \cos \chi \text{ (say)} \tag{6}$$

* Hereafter, these papers will be referred to as (1943 *a*) and (1943 *b*) respectively.

where $K = 2\pi a^2/\lambda$. Now, if A be the aperture of the beam, X_0 is evidently $= A \sin(\chi)/\lambda$, so that

$$X' = \frac{A}{\lambda} \sin \chi \left\{1 - \frac{2\pi a^2}{A} C_1'\right\} - \frac{A}{\lambda} \cos \chi \left\{\frac{2\pi a^2}{A} S'\right\}. \quad (7)$$

The above expression applies to a single droplet. Applying the method used in Section 5 of (1943 *a*), it is easily shown that the attenuation coefficient is

$$b = -4\pi a^2 N C_1' \quad (8)$$

and the refractive index, n, is given by

$$n - \mu_0 = N\lambda a^2 S' \quad (9)$$

where N is the number of droplets per unit volume. Thus, if l be the thickness of the emulsion, then the intensity of the transmitted light is

$$I = I_0 \exp[-bl] = I_0 \exp[-4\pi a^2 N l C_1'], \quad (10)$$

where I_0 is the intensity of the incident light.

The value of C_1' is given by (6). But, in the Christiansen experiment, and in the case of chromatic emulsions, the refractive indices of the two media are the same for some particular wave-length, say λ_0, and differ at other wave-lengths. The important colour effects, and other phenomena in which we are interested occur in a small range of wave-lengths about λ_0, where $(\mu - \mu_0)$ has only a very small value. Hence, the range of values of ξ that would be required will be only small, comprising of small positive and negative values. In order to be applicable for this range, C_1' can be expanded in the form of a power series in ξ as

$$C_1' = \xi^2/8 - \xi^4/144 + \cdots \quad (11)$$

so that, for small values of ξ, $C_1' = \xi^2/8$. If larger values of ξ occur in any case, expression (6) can be used.

Hence, for small values of ξ,

$$I_l/I_0 = \exp[-\pi a^2 N l \xi^2/2]. \quad (12)$$

This equation gives the variation of the intensity of the transmitted light with various factors.

Taking first the variation with ξ, it is easily seen that $I_l = I_0$ at $\xi = 0$, and decreases rapidly as ξ^2 increases, the graph connecting I_l and ξ having the shape of the well-known probability curve. Now ξ is a function of both $(\mu - \mu_0)$ and λ. But, the variation of ξ with λ is only a steady one, so that we shall at first neglect this variation, and consider only the effect of changes in the value of $(\mu - \mu_0)$. The effect of the change in the wave-length will be finally discussed.

Substituting the value for ξ, (12) becomes

$$I_l/I_0 = \exp\,[-8\pi^3 N l\,(\mu-\mu_0)^2\,a^4/\lambda^2] \qquad (13)$$
$$= \exp\,[-\gamma\,(\mu-\mu_0)^2]\ \text{(say)},$$

where
$$\gamma = 8\pi^3 N l a^4/\lambda^2. \qquad (14)$$

It is now seen that the intensity of the transmitted light is a maximum, being equal to that of the incident light for $\lambda = \lambda_0$. For both smaller and larger wave-lengths, $(\mu-\mu_0)^2$ increases, so that the intensity diminishes. Thus, only a small range of wave-lengths on either side of λ_0 is transmitted.

It is now interesting to examine how the spectral width of this region of transmission is altered by other factors. As an approximate value of the width, one may take it as equal to the range of wave-lengths, within which the intensity falls to a definite fraction (say $1/e$) of the maximum intensity. Then, $I_l/I_0 = e^{-1}$, so that the width is given by the range of wave-lengths for which

$$\gamma\,(\mu-\mu_0)^2 < 1, \text{ or } |\mu-\mu_0| < 1/\sqrt{\gamma} \qquad (15)$$

Hence, the region of transmission narrows with the increase of γ, and *vice versa*. The following results immediately follow from this:

(*a*) The region of transmission should sharpen with the increase of the thickness, *l*, of the emulsion and *vice versa*.

(*b*) As the concentration of the dispersed phase is increased, the value of N is increased, so that the spectrum of the transmitted light must become narrower, and *vice versa*.

(*c*) An emulsion containing fine particles must transmit a wider region of the spectrum than one containing coarse droplets, since *a* is smaller.

(*d*) The more widely different are the relative dispersive powers of the two media, the narrower is the spectral region transmitted. This is so, since the range of values of λ within which $(\mu-\mu_0)^2$ becomes equal to $1/\gamma$ is small, if the dispersive powers of the two media are widely different.

All these deductions from the theory have been already verified by Sogani.

In the above discussion, we have not taken the effect of the changes produced in the wave-length. Actually γ is inversely proportional to λ^2, so that it is larger for smaller wave-lengths and *vice versa*. This results in a reduction of the range of wave-lengths transmitted on the shorter wave-length side of λ_0, and in an increase on the longer wave-length side.

From (13), the value of the attenuation factor is

$$\exp\,[-8\pi^3 N l\,(\mu-\mu_0)^2\,a^4/\lambda^2].$$

Now, if one assumes a close-packing of the droplets of the dispersed phase, then the total volume occupied by them is 74 per cent. of the total volume, so that

$$N = \cdot 74/(4\pi a^3/3) = 2\cdot 22/4\pi a^3.$$

If the packing is not so close, one can introduce a coefficient σ, called the "coefficient of packing", which is equal to the ratio of the actual volume occupied by the dispersed phase to the volume it would occupy in close packing. Then, $N = 2\cdot 22\sigma/4\pi a^3$, so that attenuation factor becomes

$$\exp\left[-4\cdot 44\pi^2\sigma l\,(\mu-\mu_0)^2\,a/\lambda^2\right] = \exp\left[-22\sigma\cdot\frac{(\mu-\mu_0)^2}{\lambda^2}\,ld\right] \qquad (16)$$

where d is the diameter of the droplet.

Sogani has performed some experiments to determine the attenuation coefficient, and found that

$$I_l = I_0 \exp\left[-B\,(\mu-\mu_0)^2\,ld/\lambda^2\right]$$

which is of the same form as the one derived by us. However, for a close-packed emulsion, he found the value $B = 9$, which is much less than the theoretical value derived above. The discrepancy can partly be explained as due to the scattered light also entering the photometer, as suspected by Sogani himself, and also as due to the emulsion not being homogeneous but containing smaller droplets, both of which tend to decrease the attenuation coefficient. But it must also be noted that we have based our theory on the assumption of a random distribution of the particles, with no particular phase correlation. Such a state of affairs cannot be expected to occur in a close-packed emulsion, where one should expect the radiation from the next neighbours at least to be coherent.

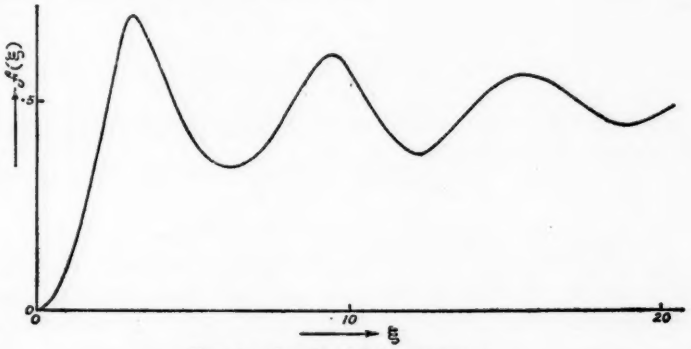


FIG. 1. Graph of $f(\xi)$ against ξ

As already remarked, the interesting phenomena exhibited by chromatic emulsions occur only for small values of ξ. An evaluation of γ for particle

sizes of about 0·003 cm., and a thickness 3 cm. of the emulsion shows that the range of values of ξ within which the light is transmitted is $|\xi| < 0{\cdot}1$. Within this range, C_1' is evidently equal to $\xi^2/8$, the other terms being extremely small. However, it is interesting to examine what happens for much larger values of ξ. For these values, the full expression for C_1' can be evaluated from (6) which gives a curve of the type shown in Fig. 1. This curve is the same as Fig. 2 of (1943 *a*), and $f(\xi)$ is the same as the present C_1'. From the figure, it is easily seen that the range of phenomena shown by chromatic emulsions lies within the initial portion of the curve, where C_1' increases with ξ. But, when $\xi > 3$, $f(\xi)$ must actually diminish with increase of ξ, so that in this range, the attenuation coefficient must diminish, and the transmission must increase with increase of ξ. This phenomenon would appear worth looking for.

Incidentally, it may be noted that, in the study of transmission of light through water droplets, one is interested in the oscillating portion of the curve, while in the present case it is the limiting portion of the curve near $\xi = 0$ that is important.

3. *Refractive Index of the Emulsion*

In the last section, we have shown that the refractive index, n, of the emulsion is given by

$$n - \mu_0 = N\lambda a^2 S' \tag{9}$$

S' can also be expanded in powers of ξ as

$$S' = \xi/3 - \xi^3/30 + \cdots \tag{17}$$

and for small values of ξ, which only occur in the region of transmission, $S' = \xi/3 = \frac{4\pi}{3}(\mu - \mu_0) \cdot \frac{a}{\lambda}$.

Hence, $$n - \mu_0 = \frac{4}{3}\pi a^3 \cdot N(\mu - \mu_0).$$

Now, $4\pi a^3 N/3$ is the total volume of the disperse phase, call it V_0, contained in unit volume of the emulsion, so that

$$n - \mu_0 = V(\mu - \mu_0), \text{ or}$$

$$n = V\mu + (1 - V)\mu_0 = V\mu + V_0\mu_0, \tag{18}$$

where V_0 is the volume of the continuous phase. This shows that the refractive index of the emulsion is the same as that of an ordinary mixture of the two liquids. This is not surprising since, when the difference in the refractive indices of the two media is small, the actual nature of the boundary is unimportant, and the optical behaviour of the emulsion is, as if the two liquids were miscible.

Differentiating (18) with respect to λ one gets

$$dn/d\lambda = V d\mu/d\mu + V_0 d\mu_0/d\lambda \tag{19}$$

which gives the relation between the dispersion of the emulsion and those of the two components.

4. *Intensity of the Diffracted Light*

The amplitude of the diffracted light is given by expressions (1) to (4), where the integrals in the expression for X_1 have to be integrated. Denoting the integrals by C and S, our aim is to integrate them for finite values of η, so as to be applicable for the case when ξ is small. The method adopted in (1943 *b*) is not suitable in this case, and a new method is therefore used for the purpose.

Expand cos (ξ cos θ) and sin (ξ cos θ) in powers of (ξ cos θ) as

$$\cos(\xi\cos\theta) = 1 - \frac{\xi^2}{(2)!}\cos^2\theta + \frac{\xi^4}{(4)!}\cos^4\theta - \cdots + (-1)^p \frac{\xi^{2p}}{(2p)!}\cos^{2p}\theta + \cdots$$

$$\sin(\xi\cos\theta) = \frac{\xi}{(1)!}\cos\theta - \frac{\xi^3}{(3)!}\cos^3\theta + \cdots + (-1)^p \frac{\xi^{2p+1}}{(2p+1)!}\cos^{2p+1}\theta + \cdots$$

Then,

$$C = \sum_{p=0}^{p=\infty} (-1)^p \frac{\xi^{2p}}{(2p)!} \int_0^{\pi/2} J_0(\eta \sin\theta) \sin\theta \cos^{2p+1}\theta \, d\theta.$$

The integral in each one of the terms of the above series can be integrated, since it is of the standard form of Sonine's first integral, *viz.*,

$$\int_0^{\pi/2} J_\mu(z \sin\theta) \sin^{\mu+1}\theta \cos^{2\nu+1}\theta \, d\theta = \frac{2^\nu \Gamma(\nu+1)}{z^{\nu+1}} \cdot J_{\mu+\nu+1}(z)$$

with $\mu = 0$ and $\nu = p$. Hence,

$$C = \sum_{p=0}^{p=\infty} (-1)^p \frac{\xi^{2p}}{(2p)!} \frac{2^p (p)!}{\eta^{p+1}} J_{p+1}(\eta). \tag{20}$$

Similarly, on expanding sin (ξ cos θ), S becomes

$$S = \sum_{p=0}^{\infty} (-1)^p \frac{\xi^{2p+1}}{(2p+1)!} \int_0^{\pi/2} J_0(\eta \sin\theta) \sin\theta \cos^{2p+2}\theta \, d\theta.$$

Here also, each one of the integrals is of the form of Sonine's integral with $\mu = 0$ and $\nu = p + 1/2$, so that

$$S = \sum_{p=0}^{\infty} (-1)^p \frac{\xi^{2p+1}}{(2p+1)!} \frac{2^{p+1/2}\,\Gamma(p+3/2)}{\eta^{p+3/2}} J_{p+3/2}(\eta) \tag{21}$$

On simplifying, and making the substitution $F_\mu(z) = J_\mu(z)/z^\mu$, we get

$$C = \sum_{p=0}^{\infty} (-1)^p \frac{2^p (p)!}{(2p)!} \xi^{2p} F_{p+1}(\eta) \tag{22}$$

$$S = \sqrt{\frac{\pi}{2}} \xi \left[\sum_{p=0}^{\infty} (-1)^p \frac{1}{2^p (p)!} \xi^{2p} F_{p+3/2}(\eta) \right]. \tag{23}$$

The amplitude X is therefore

$$X = K \sin \chi [C - F_1(\eta)] - KS \cos \chi. \tag{24}$$

But, $C - F_1(\eta)$ is easily seen to be $= \sum_{p=1}^{\infty} (-1)^p \frac{2^p (p)!}{(2p)!} \xi^{2p} F_{p+1}(\eta)$ which may be represented by $-C_1$. Then,

$$X = -KC_1 \sin \chi - KS \cos \chi. \tag{25}$$

We have thus developed X as a power series in ξ, which is convergent for all values of ξ and η (*vide* Appendix I). However, the expansion is useful only for small values of ξ, for which C_1 and S are rapidly convergent, so that the first one or two terms alone need be taken into account. Incidentally, it may be noted that on putting $\eta = 0$, C_1 and S become

$$C_1' = \xi^2/8 - \xi^4/144 + \ldots.$$
$$S' = \xi/3 - \xi^3/30 + \ldots.$$

which are identical with the values obtained by direct integration.

The intensity of the light diffracted by a single droplet is, from (25),

$$I = K^2 (C_1^2 + S^2).$$

Substituting for C_1 and S, and neglecting terms in ξ^4 and higher powers of ξ, this becomes*

$$I = \frac{\pi}{2} K^2 \xi^2 F_{3/2}^2(\eta). \tag{26}$$

The above expression relates to the intensity scattered by a single droplet in the direction ϕ. But the light reaching it, and the light diffracted by it have both to travel through the emulsion, and the total path will not differ from the thickness l of the emulsion, if ϕ is not large. Hence, the actual light coming out of the emulsion from one droplet is $I \exp(-\pi a^2 N l \xi^2/2)$. Also, if we take the droplets as distributed at random, then, the intensity of light diffracted out of unit volume of the emulsion in the direction ϕ is

$$I_\phi = N \frac{\pi}{2} K^2 \xi^2 F_{3/2}^2(\eta) \exp[-\pi a^2 N l \xi^2/2]. \tag{27}$$

---

* This expression can also be derived by introducing the approximations directly in equations (1) to (3) as shown in Appendix II.

This is the general expression for the intensity of the diffracted light. In the next two sections, we shall discuss its nature in detail.

5. *Light Diffracted by Uniform Emulsions*

In a uniform emulsion, the droplets of the dispersed phase will all be of the same size, so that a is a constant, and the only variable to be considered are the wavelength λ and the angle of scattering ϕ.

(*a*) *Variation of intensity with angle of diffraction* ϕ

If we use monochromatic light, then λ is a constant, so that ξ is fixed. Hence, I_ϕ is proportional to $F_{3/2}^2(\eta)$. This quantity is plotted in Fig. 2, from which it will be seen that the intensity is zero for $\eta = 4{\cdot}5,\ 7{\cdot}75, \ldots$. and is a maximum for $\eta = 0,\ 6{\cdot}0,\ 9{\cdot}1, \ldots$. Since $\eta = 2\pi\,(a/\lambda)\,\sin\phi$, alternate bright and dark rings must be visible in the diffraction pattern

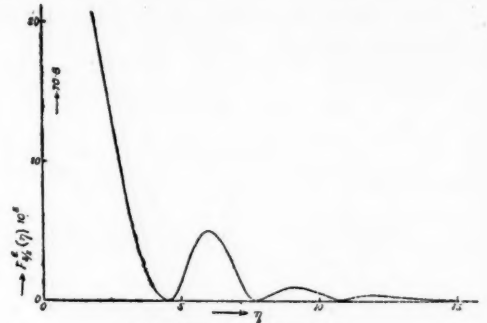


Fig. 2. Graph of $F_{3/2}^2(\eta)$ against η.

corresponding to the above values of η. The relative intensities of the first three bright rings are given by $I_1 : I_2 : I_3 = 5 : 1 : 0{\cdot}25$. For $a = 2 \times 10^{-3}$ and $\lambda = 6 \times 10^{-5}$, the angle of diffraction for the first bright ring comes out to be $\phi = 0{\cdot}028^c$. In fact, Sogani, using a homogenized emulsion, found a value $0{\cdot}025^c$ for the angular radius of the first ring. The agreement of this with the theoretical value is not to be stressed, for the type of pattern observed by Sogani had a minimum of intensity at the centre, while our theory requires a maximum. The effect observed by Sogani is similar to the diffraction of X-rays by liquids; on account of the fact that the droplets in a homogenized emulsion have a quasi-regularity in arrangement, interference effects arise in addition to the diffraction by individual droplets.

(*b*) *Variation of the Intensity with Wavelength*

From the expression (27), it is seen that the intensity $I_\phi \propto \xi^2 e^{-\beta\xi^2} F_{3/2}^2(\eta)$ where $\beta = \pi a^2 Nl/2$. Since $F_{3/2}^2(\eta)$ gives only a variation with angle, the

intensity of the ring system as a whole can be said to be proportional to $\xi^2 e^{-\beta\xi^2}$. This quantity is equal to zero at $\xi = 0$, increases with ξ up to $\xi^2 = 1/\beta$ and then decreases again. Hence, no ring system must be visible at $\lambda = \lambda_0$, for which $\xi = 0$. On either side, the rings must appear, and at first increase in intensity as the wavelength is removed more and more from λ_0, until it reaches a maximum. Thereafter, the intensity must diminish again until, when λ is far removed from λ_0, no rings must be visible. All these have been experimentally verified by Sogani.

If now, white light is used, and the spectrum of the light diffracted at an angle is observed, then the intensity will vary as $\xi^2 e^{-\beta\xi^2}$, being zero for $\lambda = \lambda_0$, and being a maximum for the values of λ for which

$$\xi^2 = 1/\beta \text{ or } (\mu - \mu_0)^2 = 1/\gamma. \tag{28}$$

The function $\xi^2 e^{-\beta\xi^2}$ has been plotted in Fig. 3 against ξ as ordinate, for the value 2 of β. This shows the nature of the intensity distribution in the spectrum of the diffracted light.

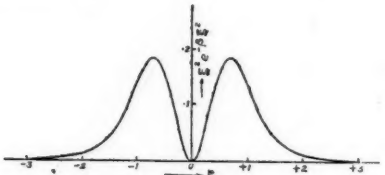


Fig. 3. Graph of $\xi^2 e^{-\beta\xi^2}$ against ξ

(*c*) *Variation of the Size of the Rings with the Wavelength*

Since $\eta = 2\pi a \sin(\phi)/\lambda$, it is evident that as λ increases, the size of the rings must increase. Thus, the width of the ring system must *continuously* increase with the wavelength, although its intensity is a minimum at λ_0, and increases on either side. This fact has also been noted by Sogani.

Another interesting fact, also noted by Sogani, is that " the size of the rings.... is, strangely enough, uninfluenced by the thickness of the emulsion". This, however, is a natural conclusion from our theory, for N and *l* occur only in the exponential in (27), and do not occur in the function $F_{3/2}^2(\eta)$, so that, for the same reason as explained in Section (4) of (1943 *b*), the size of the rings must be uninfluenced by the thickness (*l*) or the concentration (N) of the emulsion.

6. *Phenomena with Non-Uniform Emulsions*

In a non-uniform emulsion, all the droplets are not of the same size, so that the phenomena are a little complicated. In the preceding section,

it has been shown that the intensity diffracted in a direction ϕ is $\frac{\pi}{2} K^2 \xi^2 F_{3/2}^2(\eta)$. Hence, the intensity is directly proportional to the sixth power of the radius of the droplet. But the width of the bright central portion is determined by the value of η, which must be less than 4·5, *i.e.*, the range of angles covered by the central bright portion is given by $\sin \phi < 4 \cdot 5\, \lambda/2\pi a$. Thus, the width of this portion diminishes with increase of the size of the particle. Hence, it is clear that, for any angle of diffraction ϕ_1, the maximum intensity will be due to particles of a certain radius a_1 (say), those having a larger or a smaller radius, giving only a less intensity. This can be proved as follows:

If the angle of diffraction is ϕ_1, then $\eta = 2\pi \sin(\phi_1)\, a/\lambda$, and $\xi = 4\pi(\mu - \mu_0)\, a/\lambda$, so that for a particular wavelength, ξ is a constant multiple of η. Also, K is a constant multiple of ξ, so that

$$I_\phi \propto \eta^6 J_{3/2}^2(\eta)/\eta^3 \propto \eta^3 J_{3/2}^2(\eta) \tag{29}$$

Hence I_ϕ is a maximum for that value, η_0, of η for which $\eta^3 J_{3/2}^2(\eta)$ is a maximum. The radius of the droplet corresponding to this is given by $2\pi \sin(\phi_1)\, a_1/\lambda = \eta_0$, or

$$a_1 = \lambda \eta_0 / 2\pi \sin \phi_1. \tag{30}$$

Thus, for every angle ϕ_1, the predominant portion of the diffracted light is due to particles of radius a_1 given by (30), which is smaller for larger angles.

In Section 5, we have shown that the spectrum of the diffraction light always consists of a minimum at $\lambda = \lambda_0$, and two maxima on either side corresponding to

$$(\mu - \mu_0)^2_{max.} = 1/\gamma. \tag{28}$$

But γ is a function of a_1, so that it varies with the angle of diffraction in the present case. Since $\gamma = 8\pi^3 N l \cdot a^4/\lambda^2$, for an angle of diffraction ϕ_1,

$$\gamma = \frac{8\pi^3 N l\, \lambda^4\, \eta_0^4}{16\, \pi^4 \sin^4 \phi_1\, \lambda^2} = \frac{N l\, \eta_0^4\, \lambda^2}{2\pi \sin^4 \phi_1}. \tag{31}$$

Thus, other quantities being the same,

$$(\mu - \mu_0)_{max.} \propto \sin^2 \phi_1. \tag{32}$$

If, in the immediate neighbourhood of λ_0, we assume a direct proportionality between $(\mu - \mu_0)$ and $(\lambda - \lambda_0)$, then it at once follows that the spectral range between the two maxima, *viz.*,

$$2(\lambda - \lambda_0)_{max.} \propto 2(\mu - \mu_0)_{max.} \propto \sin^2 \phi_1, \tag{33}$$

Thus, as the angle of diffraction ϕ is increased, the central dark portion in the spectrum of the diffracted light must widen, and correspondingly the bright portions also must broaden. This result from the theory is remarkably confirmed by Sethi's observations, where a progressive broadening of

the spectrum was found as the direction of observation was taken further away from the incident direction.

In the discussion given above, we have neglected the effect of the variation of λ. On introducing this also, $\gamma \propto \lambda^2/\sin^4 \phi_1$, so that

$$(\mu - \mu_0)_{max.} \propto \sin^2 \phi_1/\lambda. \qquad (34)$$

Thus, the quantity $(\mu - \mu_0)_{max.}$ varies continuously with λ, being greater for smaller wavelengths. Hence, at large angles, where an appreciable portion of the spectrum is transmitted, there must be a further broadening on the shorter wavelength side, and an opposite effect on the longer wavelength side. So also, the actual intensity is proportional to λ^{-4}, which enormously increases the intensity for smaller wavelengths. For both these reasons, the spectrum must show an asymmetry, greater intensity being concentrated on the shorter wavelength side of the transmission band.

Another assumption made in the above discussion is that droplets of all sizes are present in the emulsion. Actually, there must be an upper and a lower limit to the size of the droplets. This fact limits the minimum and the maximum widths of the spectrum. Between these limits, however, the width must regularly increase with the angle of diffraction.

My sincere thanks are due to Prof. Sir C. V. Raman, for suggesting the problem and for the keen interest that he took in it.

Summary

A theory of the optical phenomena exhibited by chromatic emulsions as also those observed in the Christiansen experiment has been worked out, *de novo*, on the basis of the diffraction of light by a sphere immersed in a medium of nearly the same refractive index. Expressions are derived both for the intensity of the transmitted light, and of the light diffracted in other directions. These are discussed in relation to the intensity and the spectral nature of the light and it is shown that the theory can satisfactorily account for the various phenomena observed by Sethi and Sogani.

REFERENCES

1. Christiansen .. *Ann. d. Phys.*, 1884, **23**, 298.
2. Holmes, H. N., and Cameron, D. H. .. *Journ. Am. Chem. Soc.*, 1922, **44**, 71.
3. Ramachandran, G. N. *Proc. Ind. Acad. Sci.* **A**, 1943 *a*, **17**, 171.
4. ———— .. *Ibid.*, 1943 *b*, **17**, 202.
5. Rayleigh, Lord .. *Phil. Mag.*, 1885, **20**, 358.
6. ———— .. *Sci. Papers*, 1899, **IV**, 392.
7. Sethi, N. K. .. *Proc. Ind. Assoc. Cult. Sci.*, 1921, **6**, 124.
8. Sogani, C. M. .. *Phil. Mag.*, 1926, **1**, 321.

APPENDIX I

Note on the Convergency of the Series C_1 and S

Let $C_1 = \Sigma u_p = \sum_{p=1}^{\infty} (-1)^p \frac{2^p (p)!}{(2p)!} \xi^{2p} \frac{J_{p+1}(\eta)}{\eta^{p+1}}$.

Then $\left|\frac{u_{p+1}}{u_p}\right| = \frac{2(p+1)}{(2p+1)(2p+2)} \cdot \frac{\xi^2}{\eta} \cdot \frac{J_{p+2}(\eta)}{J_{p+1}(\eta)}$.

But, for large values of p, $J_{p+2}(\eta)/J_{p+1}(\eta) = \eta/2(p+2)$, so that

$\underset{p\to\infty}{\text{Lt}} \left|\frac{u_{p+1}}{u_p}\right| = \underset{p\to\infty}{\text{Lt}} \frac{\xi^2}{(2p+1)(2p+2)} \cdot \frac{(p+1)}{(p+2)}$ which is $= 0$, if ξ is finite.

Hence Σu_p is absolutely convergent.

In the same way, putting

$$S = \Sigma v_p = \sum_{p=0}^{\infty} (-1)^p \frac{1}{2^p (p)!} \xi^{2p+1} \frac{J_{p+3/2}(\eta)}{\eta^{p+3/2}},$$

$$\left|\frac{v_{p+1}}{v_p}\right| = \frac{1}{2p} \cdot \frac{\xi^2}{\eta} \cdot \frac{J_{p+5/2}(\eta)}{J_{p+3/2}(\eta)}.$$

Substituting the value for $J_{p+5/2}(\eta)/J_{p+3/2}(\eta)$ for large values of p, namely $\eta/(2p+5)$,

$\underset{p\to\infty}{\text{Lt}} \left|\frac{v_{p+1}}{v_p}\right| = \underset{p\to\infty}{\text{Lt}} \frac{\xi^2}{2p(2p+5)}$, which is also $= 0$, if ξ is finite.

Thus, Σv_n is also absolutely convergent.

Hence, both C_1 and S are convergent for all values of ξ and η.

APPENDIX II

A Simple Derivation of the Expression for the Intensity

As already remarked, one is interested only in small values of ξ in the study of chromatic emulsions, in which case $\cos(\xi \cos\theta) \simeq 1$ and $\sin(\xi \cos\theta) \simeq (\xi \cos\theta)$. Substituting these in (1) to (3),

$$X = K \sin\chi \left[\int_0^{\pi/2} J_1(\eta \sin\theta) \sin\theta \cos\theta \, d\theta - J_1(\eta)/\eta\right]$$

$$- K \cos\chi \int_0^{\pi/2} J_0(\eta \sin\theta)(\xi \cos\theta) \sin\theta \cos\theta \, d\theta$$

The quantity within the square brackets vanishes, and using Sonine's integral with $\mu = 0$ and $\nu = 1/2$, the second term becomes

$$-\sqrt{\frac{\pi}{2}} K \xi J_{3/2}(\eta)/\eta^{3/2},$$

Hence, the intensity is

$$I = \frac{\pi}{2} K^2 \xi^2 J_{3/2}^2(\eta)/\eta^3,$$

which is identical with expression (26).

612-43 Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent
and Published by The Indian Academy of Sciences, Bangalore.